Simplifying the conductance profiles of molecular junctions: the use of the trimethylsilylethynyl moiety as a molecule-gold contact

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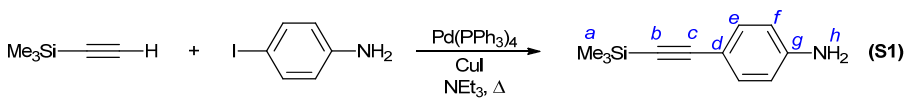
Acknowledgements

SM and PC are grateful for financial assistance from Ministerio de Ciencia e Innovación from Spain and fondos FEDER in the framework of project CTQ2009-13024. SM acknowledges his Ramón y Cajal position (RYC-2011-07869) from Ministerio de Ciencia e Innovación (Spain). HMO is grateful for financial assistance from Secretaría Nacional de Educación Superior, Ciencia, Tecnología e Innovación from Ministerio de Educación (Ecuador). VMG-S thanks Ministerio de Ciencia e Innovación (Spain) for his Ramón y Cajal position (RYC-2010-06053) and financial assistance through the grant FIS2009-07081. RJN, SJH, JAKH and PJL gratefully acknowledge funding from the EPSRC. SMG holds a PhD studentship from the EPSRC. PJL holds an EPSRC Leadership Fellowship.

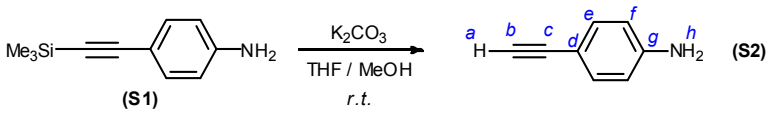
Syntheses

General Conditions All reactions were carried out in oven-dried glassware under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Triethylamine was purified by distillation from $CaSO_4$, other reaction solvents were purified and dried using Innovative Technology SPS-400 and degassed before use. The catalyst $Pd(PPh_3)_4$[1] and the five-coordinate complex $[RuCl(dppe)_2]OTf$[2] were prepared by literature methods. Other reagents were purchased commercially and used as received or prepared by variations on literature methods as described below. NMR spectra were recorded in deuterated solvent solutions on Bruker DRX-400 and Varian Inova 300, 400, 500 spectrometers and referenced against solvent resonances (^1H, ^{13}C). Atmospheric Solid Analysis Probe (ASAP) mass spectra were recorded from solid aliquots on an LCT Premier XE mass spectrometer (Waters Ltd, UK) or Xevo QToF mass spectrometer (Waters Ltd, UK) in which the aliquot is vaporized using hot N_2, ionized by a corona discharge and carried to the TOF detector (working range 100-1000 m/z). Infrared spectra were recorded on a Thermo 6700 spectrometer as Nujol mulls suspended between NaCl plates.

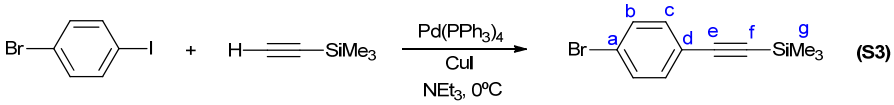


(S1)

Preparation of 4-(trimethylsilylethynyl)aniline[3] (S1). In a 100 mL Schlenk flask 4-iodoaniline (4.2 g, 20 mmol), trimethylsilylacetylene (3.5 mL, 2.4 g, 25 mmol), $Pd(PPh_3)_4$ (1.184 g, 1.025 mmol) and CuI (0.239 g, 1.256 mmol) were dissolved in anhydrous degassed NEt_3 (100 mL). The mixture was heated at reflux temperature overnight. The black suspension was taken to dryness, the residue extracted with hexane and filtered through celite. The brown solids obtained upon solvent evaporation were used in subsequent reactions without further purification. Yield 3.4 g, 18 mmol, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 9 Hz, 2H, *e*), 6.57 (d, J = 9 Hz, 2H, *f*), 3.79 (*br*. s, 2H, *h*), 0.23 (s, 9H, *a*). ^{13}C NMR {^{1}H} (101 MHz, $CDCl_3$) 146.9 (*d*), 133.5 (*f*), 114.7 (*e*), 112.6 (*g*), 106.1, 91.5 (*b/c*), 0.3 (*a*).

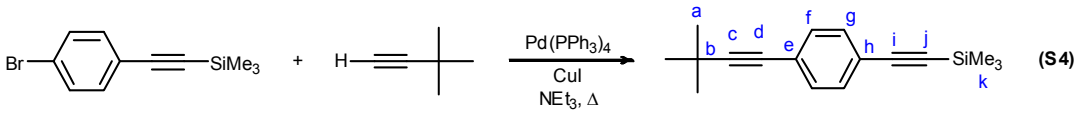


Preparation of 4-ethynylaniline[3] (S2). To a solution of 4-(trimethylsilylethynyl) aniline **(S1)** (3.25 g, 17.16 mmol) in THF/MeOH (1:1, 100 mL), K_2CO_3 (3.5 g, 25 mmol) was added and the resulting suspension stirred at room temperature overnight. The solution was then taken to dryness under reduced pressure. The residue was extracted with CH_2Cl_2 and filtered through basic alumina (Brockmann III). The orange precipitate formed upon addition of hexane to the filtrate was collected by filtration and dried in air. Yield 1.9 g, 16.2 mmol, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 9 Hz, 2H, *e*), 6.59 (d, J = 9 Hz, 2H, *f*), 3.82 (s, 2H, *h*), 2.96 (s, 1H, *a*). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.1 (*d*), 133.6 (*f*), 114.7 (*e*), 111.4 (*g*), 84.5, 75.0 (*b/c*). MS^+ (ASAP) (*m/z*) 233.1 (100, $[2M+H]^+$), 118.1 (60, $[M+H]^+$).). IR (*nujol)*: 3486, 3389 cm^{-1} ν(-NH_2), 3258 cm^{-1} ν(C_{sp}−H), 2098 cm^{-1} ν(C≡C).

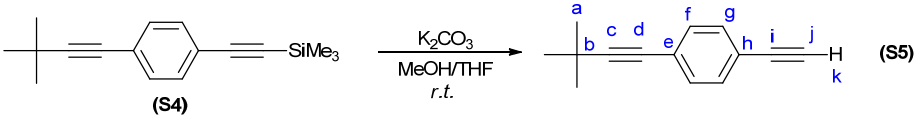


Preparation of 4-bromo-(trimethylsilylethynyl)benzene[4] (S3). To a 500 mL round Schlenk flask immersed in an ice bath and charged with NEt_3 (250 mL), 4-iodo-bromobenzene (18.05 g, 63.80 mmol), $Pd(PPh_3)_4$ (1.85 g, 1.60 mmol) and CuI (0.30 g, 1.6 mmol) were added. To the cooled solution trimethylsilylacetylene (11.0 mL, 7.51 g, 76.5 mmol) was added drop wise. The mixture was stirred in an ice bath for 8 h. Upon completion of the reaction the brown suspension was taken to dryness under reduced pressure and the residue was purified by silica gel column chromatography (hexane). Removal of solvent from

the main fraction yielded a colourless oil that crystallized on standing. Yield 15.9 g, 62.8 mmol, 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 9 Hz, 2H, *c*), 7.32 (d, J = 9 Hz, 2H, *b*), 0.24 (s, 9H, *g*). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.5, 131.6 (*b/c*), 122.9, 122.3 (*a/d*), 104.0 (*f*), 95.7 (*e*), 0.0 (*g*). MS^{+} (ASAP) (*m/z*) 505.9 (100, [2M-2H]$^{+}$), 253.9 (41.8, [M]$^{+}$).

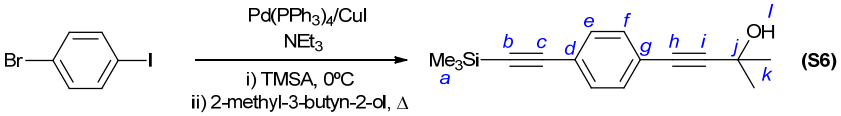


Preparation of ((4-(3,3-dimethylbut-1-yn-yl)phenyl)ethynyl)trimethylsilane (S4). To a 100 mL oven-dried Schlenk flask charged with ((4-bromophenyl)ethynyl) trimethylsilane **(S3)** (2.53 g, 9.99 mmol), $Pd(PPh_3)_4$ (0.60 g, 0.52 mmol) and CuI (0.30 g, 0.52 mmol) in NEt_3 (100 mL), 3,3-dimethylbut-1-yne (1.53 mL, 1.02 g, 12.4 mmol) was added. The mixture was stirred at reflux overnight. The brown suspension was filtered and the red filtrate taken to dryness under reduced pressure. The residue was purified through a silica gel column using hexane as eluent. The pure product was obtained as an off-white powder upon solvent evaporation of the main fraction. Yield 2.16 g, 8.49 mmol, 85.4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 9 Hz, 2H, *g*), 7.31 (d, J = 9 Hz, 2H, *f*), 1.32 (s, 9H, *a*), 0.25 (s, 9H, *k*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 133.8, 131.5 (*e/h*), 122.4, 122.1 (*i/j*), 105.0, 100.7, 95.6 (*d/i/j*), 79.0 (*c*), 31.1 (*a*), 28.2 (b) 0.1 (*k*).

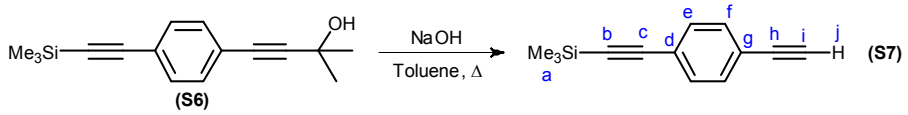


Preparation of 1-(3,3-dimethylbut-1-yn-1-yl)-4-ethynylbenzene (S5). To a 250 mL round bottomed flask charged with a solution of methyl ((4-(3,3-dimethylbut-1-yn-1-yl)phenyl)ethynyl)trimethylsilane **(S4)** (1.5 g, 5.9 mmol) in MeOH/THF (1:1) (100 mL), K_2CO_3 (0.83 g, 6.0 mmol) and the suspension was stirred at room temperature overnight. The solution was then filtered and the filtrate taken to dryness under reduced pressure. The resultant black oil was re-dissolved in Et_2O (50 mL) and washed with water (2×50 mL) and brine (1×50 mL) and dried over $MgSO_4$. Removal of solvent yielded the pure product as a

yellowish oil. Yield 1.0 g, 5.5 mmol, 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 9 Hz, 2H, *g*), 7.56 (d, J = 9 Hz, 2H, *f*), 3.13 (s, 1H, *k*), 1.31 (s, 9H, *a*). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.0, 131.6 (*f/g*), 124.9, 121.1 (*e/h*), 100.9, 83.6, 78.9, 78.4 (*c/d/i/j*), 31.1 (*a*), 28.2 (b).

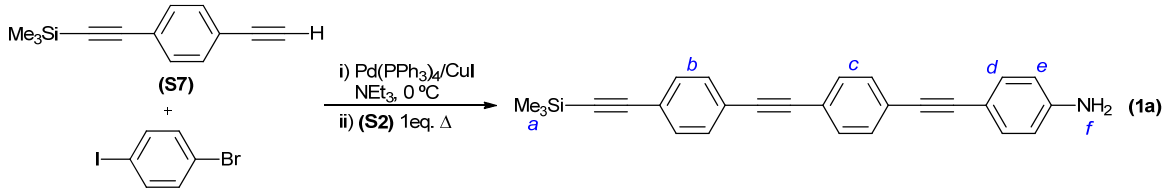


Preparation of 2-methyl-4-(4-((trimethylsilyl)ethynyl)phenyl)but-3-yn-2-ol[5] (S6). To a 500 mL Schlenk flask immersed in an ice bath and charged with NEt_3 (450 mL), 1-bromo-4-iodobenzene (30.01 g, 106.1 mmol), $Pd(PPh_3)_4$ (6.12 g, 5.30 mmol) and CuI (1.01 g, 5.30 mmol) were added. To the cooled suspension, trimethylsilylacetylene (16.5 mL, 11.4 g, 116 mmol) was added in small portions over an hour. After stirring the solution at 0 ºC for 6 h, trimethylsilylacetylene excess was removed under reduced pressure keeping the reaction vessel in the ice bath. After refilling the vessel with N_2, 2-methyl-3-butyn-2-ol (11.3 mL, 9.81 g, 116 mmol) was added and the reaction mixture was taken out of the ice bath and heated at reflux overnight. The reaction mixture was then taken to dryness under reduced pressure, and the resulting black residue was re-dissolved in CH_2Cl_2 and adsorbed onto silica for further silica gel column chromatography (hexane). The pure product was collected upon solvent evaporation of the main fraction as a yellow powder. Yield 21 g, 83 mmol, 78 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 9 Hz, 2H, *e*), 7.31 (d, J = 9 Hz, 2H, *f*), 1.32 (s, 6H, *k*), 2.01 (s, 1H, *l*), 0.25 (s, 9H, *a*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.8, 131.5 (*e/f*), 123.0, 122.9 (*d/g*), 104.7 (*b*), 96.2, 95.8, 81.8 (*c/h/i*), 65.7 (*j*), 31.51 (*k*), 0.0 (*a*). MS^{+} (ASAP) (*m/z*) 241.10 (100, $[M\text{-}OH]^{+}$).

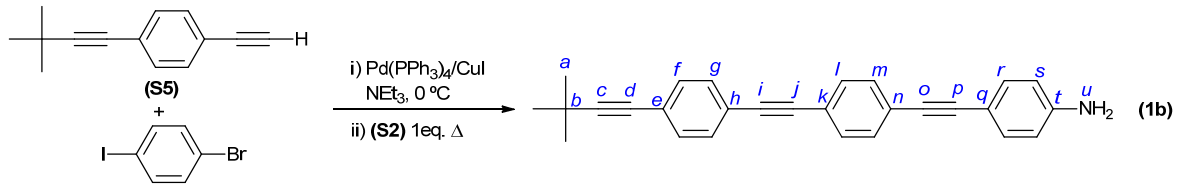


Preparation of 1-ethynyl-4-(trimethylsilylethynyl)benzene[5] (S7). A 250 mL round bottom flask, fitted with a nitrogen purge, reflux condenser and bubbler was charged with sodium hydroxide (0.63 g, 0.16 mmol), 2-methyl-4-(4-((trimethylsilyl)ethynyl) phenyl)but-3-

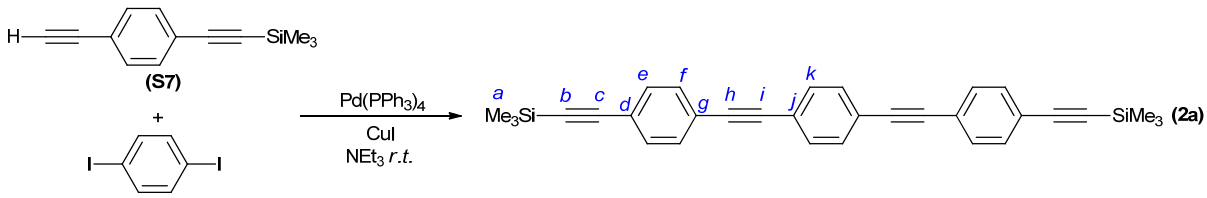
yn-2-ol **(S6)** (3.25 g, 12.6 mmol) and anhydrous toluene (150 mL). The solution was heated at reflux for 30 min whilst nitrogen was bubbled through it. Upon completion of the reaction, the red solution was poured into water, and the organic phase was washed with water (2×150 mL) and brine (1×150 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane:CH_2Cl_2 (9:1) as the eluent. Removal of solvent from the main fraction yielded the pure product as a white solid. Yield 1.83 g, 9.23 mmol, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 4H, *e/f*), 3.16 (s, 1H, *j*), 0.25 (s, 9H, *a*). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 132.1, 132.0 (*e/f*), 123.7, 122.2 (*d/g*), 104.5 (*b*), 96.6 (*c*), 83.3 (*h*), 79.1 (*i*), 0.0 (*a*). MS-ASAP$^+$ (*m/z*) 183.05 (100, [M-CH_3]$^+$), 198.07 (24.4, [M]$^+$).



Preparation of 4-((4-((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl) ethynyl)aniline[3] (1a). To a 100 mL Schlenk flask charged with NEt_3 (70 mL), immersed in an ice bath, 1-ethynyl-4-(trimethylsilylethynyl)benzene **(S7)** (0.15 g, 0.76 mmol), $Pd(PPh_3)_4$ (0.04 g, 0.04 mmol) and CuI (0.01 g, 0.05 mmol) were added. To the cooled mixture, 1-bromo-4-iodobenzene (0.22 g, 0.78 mmol) was added. After stirring the solution at 0 ºC for 5 h, 4-ethynylaniline **(S2)** (0.09 g, 0.77 mmol) was added and the reaction mixture was taken out of the ice bath and heated at reflux overnight. Upon completion of the reaction, the precipitate was removed by filtration and the yellow filtrate taken to dryness under reduced pressure. The resulting yellow residue was then purified by column chromatography in neutral alumina (hexane:EtOAc) (6:4). The orange solid obtained from taking the appropriate fraction to dryness was crystallised from hot toluene giving the pure product as a yellow powder. Yield 0.09 g, 0.23 mmol, 30 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 4H, *b*), 7.44 (s, 4H, *c*), 7.34 (d, *J* = 9 Hz, 2H, *d*), 6.64 (d, *J* = 9 Hz, 2H, *e*), 3.85 (s *br.*, 2H, *f*), 0.25 (s, 9H, *a*). MS$^+$ (ASAP) (*m/z*) 389.2 (100, [*M*]$^+$). IR (*nujol*): 3445, 3363, 3215 *ν*(N−H), 2200, 2139, 2173 cm^{-1} *ν*(C≡C).

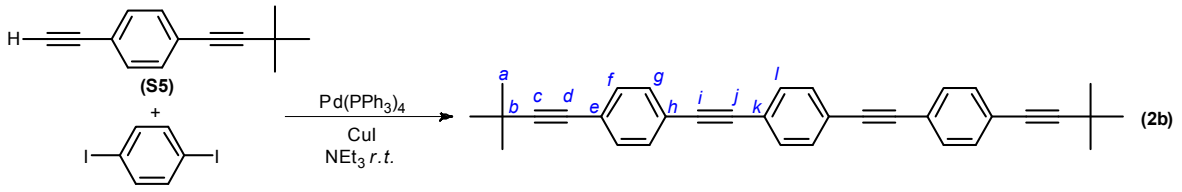


Preparation of 4-((4-((4-(3,3-dimethylbut-1-ynyl)phenyl)ethynyl)phenyl) ethynyl)aniline (1b). To a 100 mL Schlenk flask immersed in an ice bath and charged with NEt_3 (90 mL), 1-ethynyl-4-(3,3-dimethylbut-1-ynyl)benzene **(S5)** (0.20 g, 1.10 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.06 mmol) and CuI (0.01 g, 0.06 mmol) were added. To the cooled solution 1-bromo-4-iodobenzene (0.25 g, 0.89 mmol) was added. After stirring the mixture at 0 ºC for 4 h, 4-ethynylaniline **(S2)** (0.11 g, 0.94 mmol) was added and the reaction vessel was out of the ice bath and heated at reflux overnight. Upon completion of the reaction, the precipitate was removed by filtration and the yellow filtrate was then taken to dryness under reduced pressure. The resulting orange residue was then purified by column chromatography in neutral alumina (hexane:EtOAc) (9:1). The orange solid obtained from taking the appropriate fraction to dryness was then crystallised from toluene and washed with Et_2O (5 mL). The pure product was obtained as a pale yellow powder. Yield 0.05 g, 0.23 mmol, 15 %.^{1}H NMR (700 MHz, $CDCl_3$) δ 7.46 (s, 4H, *l/m*), 7.43 (d, J = 8 Hz, 2H, *r*), 7.36, 7.34 (d, d, J = 8 Hz, 2H, 2H, *f/g*), 3.84 (s br, 2H, *u*), 1.32 (s, 9H, *a*). ^{13}C NMR {^{1}H} (176 MHz, $CDCl_3$) δ 147 (*t*), 133.2 (s), 131.7, 131.6, 131.5, 131.4 (*g/l/m/r*), 124.3, 124.1, 122.4, 122.2 (*h/k/n/q*), 114.9 (*s*), 100.8 (*c*), 92.4, 90.9, 90.7, 87.3 (*i/j/o/p*), 79.0 (*d*), 31.1 (*a*), 28.2 (*b*). MS$^+$ (ASAP) (*m/z*) 373.2 (100, $[M]^+$).

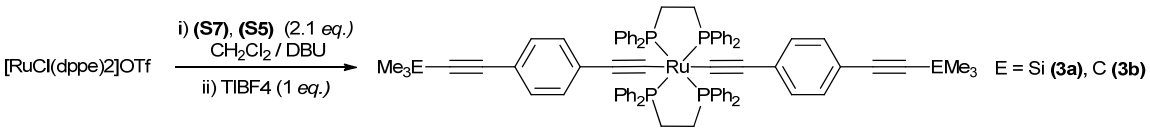


Preparation of 1, 4-bis((4-((trimethylsilyl)ethynyl)phenyl)ethynyl)benzene[6] (2a). A 25 mL Schlenk flask charged with NEt_3 (20 mL), 1-ethynyl-4-(trimethylsilylethynyl)benzene **(S7)** (0.37 g, 1.5 mmol), 1, 4-diiodobenzene (0.23 g, 0.70 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.10 mmol) and CuI (0.02 g, 0.10 mmol) were added and the resulting suspension stirred at room temperature overnight. The precipitate was collected by filtration and washed thoroughly with hexane. The product was then recrystallized from toluene yielding the pure product as white needles. Yield 0.13 g, 0.28 mmol, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 4H, *e*), 7.45 (s br, 8H, *f/k*), 0.26 (s, 18H, *a*). ^{13}C {^{1}H} NMR

(101 MHz, $CDCl_3$) δ 132.1, 131.7, 131.6 (e/*f*/*k*), 123.4, 123.2, 123.2 (*d*/*g*/*j*), 104.8 (*b*), 96.6 (*c*), 91.2, 91.1 (*h*/*i*), 0.1 (*a*). MS^+ (ASAP) (*m/z*) 470.20 (100, $[M]^+$).



Preparation of 1, 4-bis((4-((3, 3-dimethylbut-1-ynyl)phenyl)ethynyl)benzene (2b). To a 25 mL Schlenk charged with NEt_3 (20 mL), 1-ethynyl-4-(3, 3-dimethylbut-1-ynyl)benzene **(S5)** (0.37 g, 1.5 mmol), 1, 4-diiodobenzene (0.25 g, 0.76 mmol), $Pd(PPh_3)_4$ (0.05 g, 0.04 mmol) and CuI (0.01 g, 0.05 mmol) were added and the mixture stirred at room temperature overnight. The white precipitate was collected by filtration and washed with hexane. The product was then crystallized from hot toluene and washed with hexane and EtOH to obtain the pure product as white needles. Yield 0.24 g, 0.56 mmol, 74%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 4H, *l*), 7.44 (d, *J* = 8 Hz, 4H, *f*), 7.36 (d, *J* = 8 Hz, 4H, *g*), 1.32 (s, 18H, *a*). ^{13}C $\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 131.7, 131.7, 131.5 (*f*/*g*/*l*), 124.4, 123.2, 122.0 (*e*/*h*/*k*), 100.9 (*c*), 91.3, 90.5 (*i*/*j*), 79.0 (*d*), 31.1 (*a*), 28.2 (*b*). MS^+ (ASAP) (*m/z*) 389.2 (100, $[M]^+$).



General procedure for the preparation of bis(dppe)-bis(ethynyl) Ruthenium (II) complexes:

To a solution of $[RuCl(dppe)_2]OTf$ (0.100 g, 0.092 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (*excess*) in dry degassed CH_2Cl_2 (4 mL), slight excess of the appropriate alkyne (0.20 mmol) was added. The resulting red solution typically turned yellow after stirring at room temperature for 1h. To the yellow solution, one equivalent of $TlBF_4$ (0.027 g, 0.092 mmol) was added and the suspension stirred for 15 minutes. The off-white precipitate (TlCl) was carefully removed by filtration through neutral alumina (Brockmann I) and rinsed thoroughly with CH_2Cl_2. Solution volume was reduced upon solvent evaporation (2 mL) and the final products **(3a, 3b)** were obtained as a pale-yellow

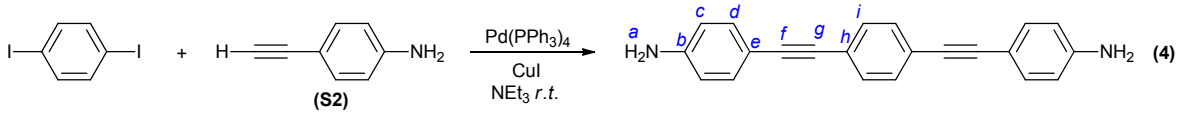
precipitate upon addition of Et_2O. Single crystals were obtained from the appropriate solvent mixture (*vide infra*).

***trans*-Ru(C≡C–C_6H_4–C≡C–$SiMe_3$-4)$_2$(dppe)$_2$ (3a)**

(96 mg, 81%). Single crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 16H), 7.25 (d, *J* = 8 Hz, 4H), 7.15 (m, 8H), 6.92 (m, 16H), 6.62 (d, *J* = 8 Hz, 4H), 2.61 (m, 8H), 0.26 (s, 9H). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 52.4 (s, *dppe*). IR (*nujol)*: 2153 cm^{-1} *ν*(Si–C≡C), 2065 cm^{-1} *ν*(Ru–C≡C).

***trans*-Ru(C≡C–C_6H_4–C≡C–CMe_3-4)$_2$(dppe)$_2$ (3b)**

(96 mg, 83%). Single crystals suitable for X-ray diffraction were obtained from $CHCl_3$/MeOH. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.43 (m, 16H), 7.20-7.10 (m, 12H), 6.96-6.88 (m, 16H), 6.63 (d, *J* = 8 Hz, 4H), 2.61 (t, *J* = 8 Hz, 8H), 1.33 (s, 18H). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$) δ 52.5 (s, *dppe*). IR (*nujol)*: 2067 cm^{-1} *ν*(C≡C).



Preparation of 4-4'-(1, 4-phenylenebis(ethyne-2,1-dyl))dianiline[3] (4). To a 100 mL Schlenk charged with NEt_3 (80 mL), 4-ethynylaniline **(S2)** (0.37 g, 3.2 mmol), 1, 4-diiodobenzene (0.53 g, 1.6 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.10 mmol) and CuI (0.02 g, 0.10 mmol) were added and the mixture stirred at room temperature overnight. The orange precipitate was collected by filtration washed thoroughly with hexane and purified by column chromatography in neutral alumina (hexane:EtOAc) (*4:6*). The brown powder obtained was then crystallized from hot toluene to obtain the pure product as orange needles. Yield 0.074 g, 0.239 mmol, 15.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 4H, *i*), 7.33 (d, *J* = 9 Hz, 4H, *d*), 6.63 (d, *J* = 9 Hz, 4H, *c*), 3.82 (s br, 4H, *a*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9 (*b*), 133.2, 131.3 (*d/i*), 123.3, 112.7 (*e/h*), 114.9 (*c*), 92.0, 87.5 (*f/g*). MS$^+$ (ASAP) (*m/z*) 309.15 (100, $[M+H]^+$).

Details of the *I*(*s*) measurements

In the *I*(*s*) technique (*I* = current and *s* = distance) the STM tip is located at a fixed distance above the gold surface which has been functionalized with the molecular target. To perform the measurements the feedback loop is disabled for a short time period and the current is recorded as the STM tip is retracted until the molecule junction(s) break. When molecular bridge formation occurs the current-distance curve generally features a current plateau followed by a rapid drop in current.[7, 8] In the *I*(*s*) technique contact between the gold STM tip and the surface is avoided, i.e. no metallic break junction is formed. The distinctive current plateaus point to the formation of molecular bridges between the gold substrate surface and gold STM tip. By contrast, the current simply decreases nearly exponentially with tip–sample separation when molecular bridges are not formed during the tip retraction.. Current-distance curves recorded by the *I*(*s*) method are statistically analyzed by constructing histogram plots. From these histograms the single molecule conductance is determined. Exponential decay curves characteristic of tunneling in the absence of molecular bridge formation and other indistinct curves were rejected from histogram analysis. Conductance data are presented in units of the conductance quantum $G_0 = 2e^2/h = 77.4$ μS for $U_t = 0.6$ V. For calculating errors, Gaussian curves are used to fit peaks in the histograms.

Immediately prior to use gold on glass slides (Arrandee®, Schroeer, Germany) were heated in the flame of a Bunsen burner ("flame-annealing"). During this process the slide took on a slight orange colour and it was kept in this state for around 30 seconds. This procedure is known to result in atomically flat Au(111) terraces.[9] All compounds were then adsorbed by immersion of their solutions in THF (0.05 mM) for about 40 seconds. The low concentrations and relatively short immersion times are aimed at promoting low surface coverage of the molecular target on the gold slide, consequently promoting single molecule events in favour of the formation of multiple molecular bridges. After adsorption, the sample was rinsed in ethanol and then blown dry in a stream of N_2 gas. Gold STM tips were freshly prepared for each experiment by etching of a 0.25 mm Au wire (99.99%) in a mixture of HCl (50%) and ethanol (50%) at +2.4 V.[9]

Single Molecule Conductance for **4** and **1a**

Figure S1 shows typical conductance curves observed in the presence both of **4** (a, left) and **1a** (b, left) using the *I(s)* technique. These data curves are presented with the tunneling conductance on the y-axis and distance displacement on the x-axis (distance

displacement from the set-point distance from which the tip is retracted following disengagement of the feedback loop). These curves exhibit typical current steps which are attributed to the breaking of molecular bridges that were attached between tip and sample at the start of the tip retraction scan. Two different fundamental types of current jumps can be observed in these curves. One group occurs at conductance values of 3.20±0.83 x 10^{-5} G_0 for **4** (figure S2a, right side) and at 2.99±0.43 x 10^{-5} G_0 for **1a** (figure S3b, right side); and another group at conductance values of 14.4±2.78 x 10^{-5} G_0 and 7.92±1.33 x 10^{-5} G_0, respectively. These two groups dominate the histograms showed in Figure S1 right side, which were taken at different randomly selected locations of the sample. The lower conductance peak will be referred to as ***A*** ("low" conductance), whereas the higher conductance peak will be referred to as ***B*** ("medium" conductance).

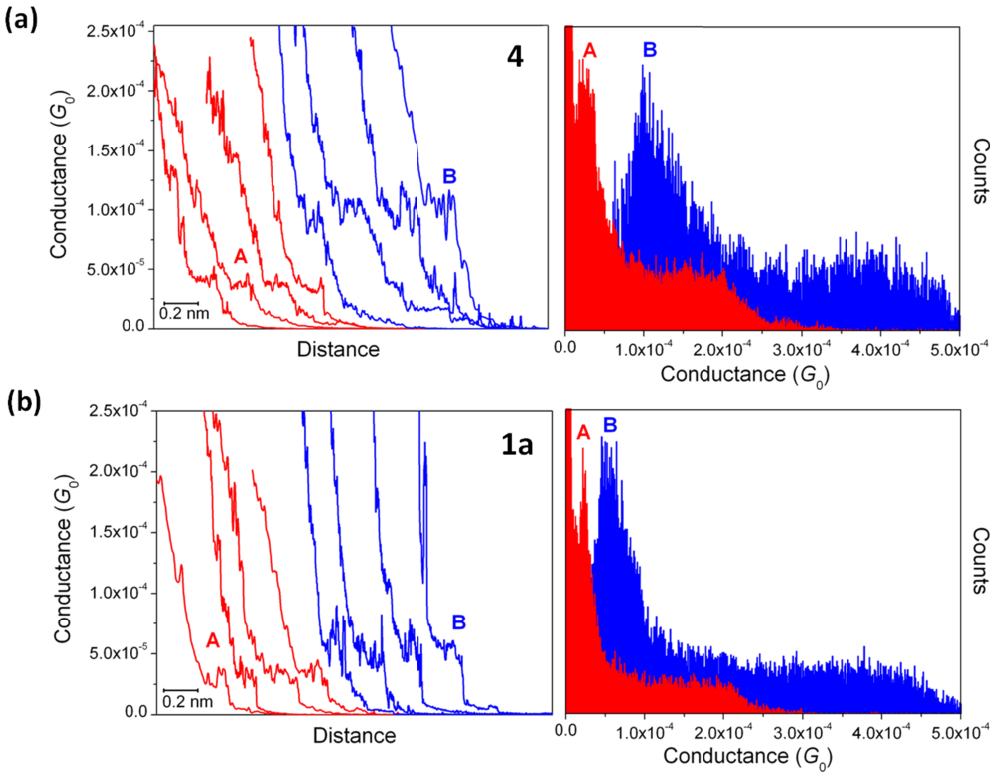


Figure S1. Typical conductance traces (left side) and histograms (right side) recorded using the *I(s)* technique for (a) **4** and (b) **1a**. The curves are shifted horizontally for clarity, and conductance histograms built by adding together all the points of conductance traces that showed discernible plateaus. Conductance data are presented in units of the conductance quantum $G_0 = 2e^2/h = 77.5$ μS. $U_t = 0.6$ V.

XPS measurements

X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Kratos AXIS ultra DLD spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV) using a pass

energy of 20 eV. The photoelectron take off angle was 90º with respect to the sample plane. To provide a precise energy calibration, the XPS binding energies were referenced to the C1s peak at 284.6 eV. Figure S2a and S2b show XPS measurements on **2a** and **3a** as both powders and SAMs, respectively. For preparing SAMs, gold on glass slides were incubated in 0.01 mM solutions of **2a** and **3a** in $CHCl_3$ for 24 h. Afterwards the substrates were thoroughly rinsed with $CHCl_3$ and then blown dry in a stream of nitrogen gas.

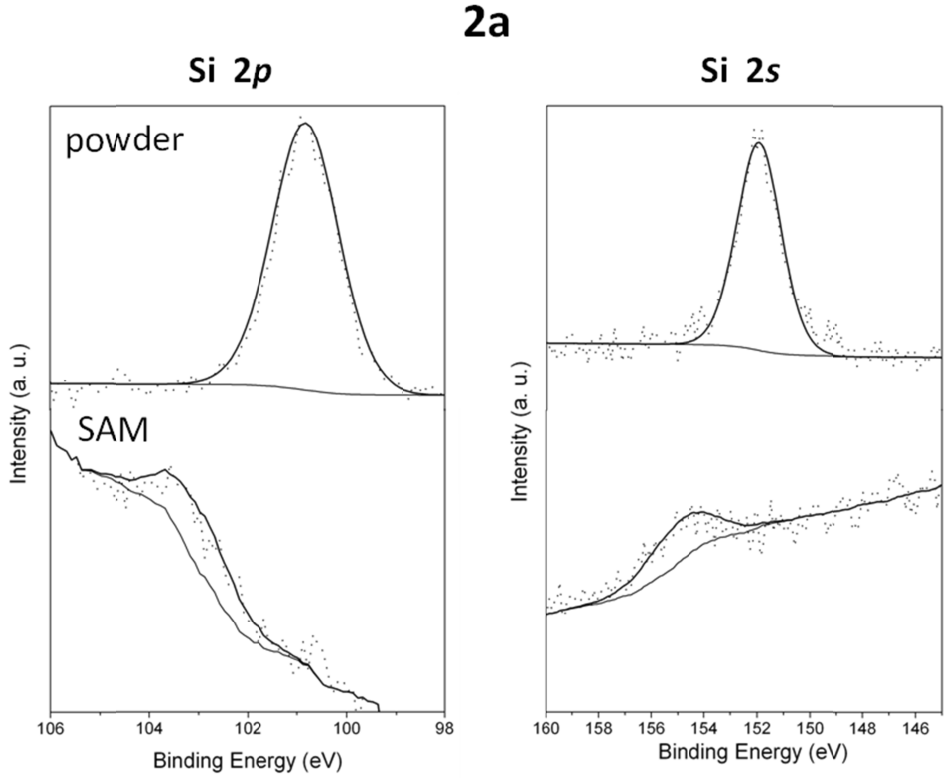


Figure S2a. XPS spectra of the Si 2p (left) and Si 2s (right) region for the powder (top), and for a SAM (bottom) for the compound **2a**.

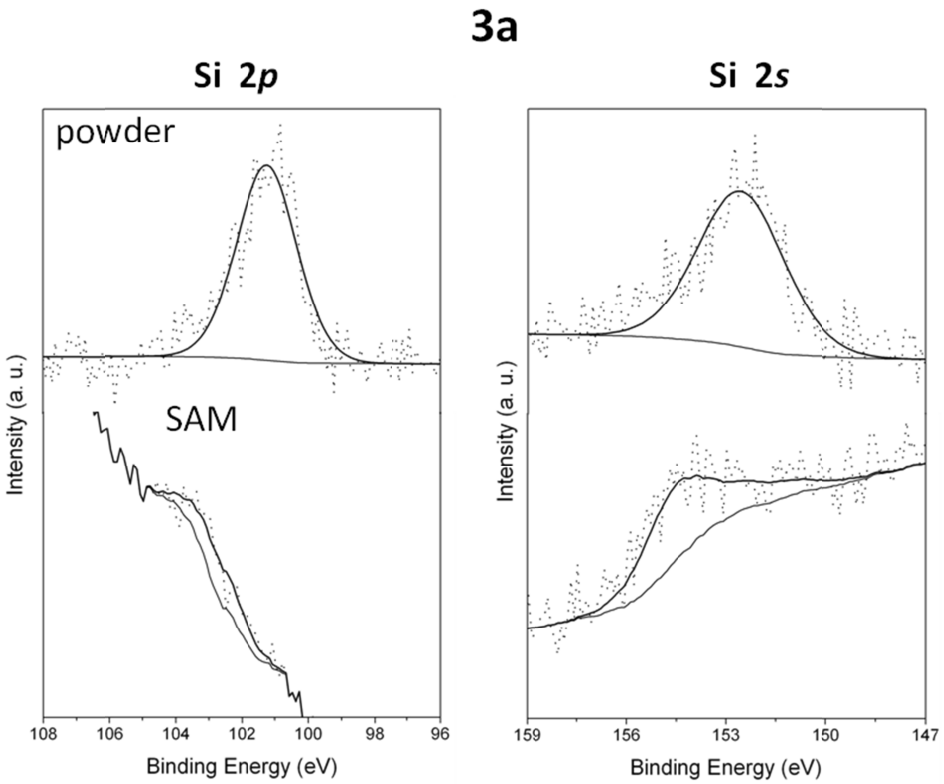


Figure S2a. XPS spectra of the Si 2p (left) and Si 2s (right) region for the powder (top), and for a SAM (bottom) for the compound **3a**.

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