Supporting Information

Methods

Chemicals: Chloroauric Acid [HAuCl$_4$·4H$_2$O], ammonium chloride and acetone were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Dicyandiamide (C$_2$H$_4$N$_4$) and was purchased from Alfa Aesar. Ar/H$_2$ (5%) was purchased from Linde Gas. The water used in all experiments was ultrapure (18.2 MΩ). All chemicals were used as received without further purification.

Syntheis of g-C$_3$N$_4$ nanosheets: 1 g dicyandiamide and 10 g NH$_4$Cl were put together into a 50 mL ceramic crucible, then shake to mix as evenly as possible. The mixture was heated under air at 2.3 °C min^{-1} (4h) up to 550 °C and then treated at 550 °C for 2h. The yellow and fluffy powder is obtained after the temperature dropped.

Synthesis of Au/g-C$_3$N$_4$ nanosheets

The Au$_1$/g-C$_3$N$_4$ nanosheets were prepared based on previously reported method[1,2]. The HAuCl$_4$ (0.1g mL^{-1}) was added into the g-C$_3$N$_4$ aqueous dispersion (200 mg g-C$_3$N$_4$ dispersed in 50 mL of distilled water) and keeping stirring at room temperature for 12 h. The resulting product was washed with distilled water several times, and was then dried in vacuum at 50 °C overnight to give HAuCl$_4$/g-C$_3$N$_4$ sample, followed by annealing at 110 °C in H$_2$/Ar (5%) atmosphere for 2 h to give Au$_1$/g-C$_3$N$_4$ sample. When the temperature is higher than 130 °C, the Au$_{1+NPs}$ samples was obtained.

Synthesis of Au NPs/g-C$_3$N$_4$ nanosheets

The Au nanoparticles were prepared based on previously reported method[3,4]. In a typical preparation of Au nanoparticles, 0.1 g/mL aqueous HAuCl$_4$ (200 ⏴l) was dissolved in OAm (10 mL)

at 60 °C under vigorous stirring for 10 min. Then, a solution of borane-tert-butylamine (100 mg, 1.15 mmol) in OAm (1 mL) was added quickly into the previous solution, and the reaction mixture immediately turned red. After 1 min, the flask was heated to 80 °C for a further 1 hour. After cooling to room temperature, the solution was washed with ethanol (40 mL) and then dispersed in cyclohexane for future use. For the preparation of Au NPs/g-C_3N_4 catalyst, g-C_3N_4 nanosheets are added into the dispersions of Au at a loading of 0.3 wt. % (based on Au), and the mixtures are stirred overnight. The catalysts are obtained through centrifugation and drying under vacuum. In order to remove the surfactant from the surface of gold nanoparticles, we calcined at 400 °C for 2 hours in an argon atmosphere tubular furnace.

Characterization

The crystalline structure and phase purity were determined by Rigaku RU-200b X-ray powder diffractometer with Cu Ka radiation (I = 1.5418 Å). The size and morphology of as-synthesized samples were determined by using Hitachi-7700 transmission electron microscope working at 100 kV. The high-angle annular dark-field scanning TEM (HAADF-STEM) were operated at 200 kV by a JEOL-ARM200F. The composition of the product was measured by the inductively coupled plasma-atomic emission spectrometry and energy dispersive X-ray spectrometer.

Photoemission spectroscopy experiments (XPS) were performed on a ULVAC PHI Quantera microprobe in Beijing, China. The end station is comprised of four ultrahigh vacuum (UHV) chambers including analysis chamber, preparation chamber, molecular beam epitaxy (MBE) chamber, and a radial distribution chamber (RDC). The base pressures are 7×10^{-11}, 1×10^{-10}, 5×10^{-10} and 2×10^{-11} mbar, respectively. In addition, a quick sample load-lock system is attached to the RDC. The analysis chamber is equipped with a VG Scienta R4000 analyzer and a monochromatic Al

Ka X-ray source. The sample was annealed at the preparation chamber and then transferred to the analysis chamber for characterization. The core-level spectra were measured using a monochromatic Al Ka X-ray source. For the core-level spectra, the binding energies were calibrated using the C 1s feature located at 284.6 eV as the reference.

X-ray absorption data collection and analysis

The Au L3-edge X-ray absorption spectra were collected at room temperature in fluorescence mode at beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) using a Si (111) double-crystal monochromator. The storage rings of BSRF were operated at 2.5 GeV with a maximum current of 250 mA in decay mode. The energy was calibrated using Au foil, while the incident and fluorescence x-ray intensities were monitored by using standard 25% Ar and 75% N_2-filled ion

$$\chi(k) = \sum_j \frac{N_j S_o^2 F_j(k)}{k R_j^2} \exp[-2 k^2 \sigma_j^2] \exp[\frac{-2 R_j}{\lambda(k)}] \sin[2k R_j + \phi_j(k)]$$

chamber and Ar-filled Lytle-type detector, respectively. A detuning of about 20% by misaligning the silicon crystals was also performed to suppress the high harmonic content. The samples were pelletized as disks of 13 mm diameter with 1mm thickness before measurements.

The XAFS raw data were background-subtracted, normalized, and Fourier transformed by the standard procedures with the ATHENA program. To obtain the quantitative structural parameters around the absorbing Au atoms, least-squares curve fitting analysis of the EXAFS χ(k) data was performed using the ARTEMIS package, with the theoretical scattering amplitudes, phase shifts and the photoelectron mean free path for all paths calculated by FEFF6.

The following EXAFS equation was used:

where S_0^2 is the amplitude reduction factor, $F_j(k)$ is the effective curved-wave backscattering amplitude, N_j is the number of neighbors in the jth atomic shell, R_j is the distance between the X-

ray absorbing central atom and the atoms in the jth atomic shell (backscatterer), λ is the mean free path in Å, $\varphi_j(k)$ is the phase shift (including the phase shift for each shell and the total central atom phase shift), σ_j is the Debye-Waller parameter of the jth atomic shell (variation of distances around the average R_j). . In present work, the variable parameters that are determined by using the EXAFS equation to fit the experimental data include N, R, and the EXAFS Debye-Waller factor (σ^2). S_0^2 was determined in the fit of Au standard to be 0.85, and used as fixed value in the rest of the EXAFS models. For Au L_3-edge, E_0 was defined as 11921 eV for the scale conversion from the photo energy (eV) to the wave vector (k, Å^{-1}). All fits were performed in the R space with k-weight of 3. The EXAFS R-factor (R_f) that measures the percentage misfit of the theory to the data was used to evaluate the goodness of the fit.

Procedure for hydrosilylation of phenylacetylene: In a typical reaction, a 10 mL Schlenk tube was charged with 0.5 mmol phenylacetylene, 0.75 mmol silane, 60 mg Au$_1$/g-C$_3$N$_4$ catalyst and 5 mL solvent under nitrogen atmosphere. After stirring the result mixture under specific temperature and time, the catalyst was removed through centrifugation. GC-FID (SP-6890) and GC-MS was used to determine the conversion and selectivity. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ on a Bruker Avance 500 MHz Spectrometer at 298 K.

Procedure for recovering and reusing the catalyst: The reaction mixture was centrifuged under 9900 r/min after the reaction was over. Then the supernatant was removed and the residue was washed with acetone (3×5 mL). The recovered Au catalyst was used directly for the next run of the model reaction.
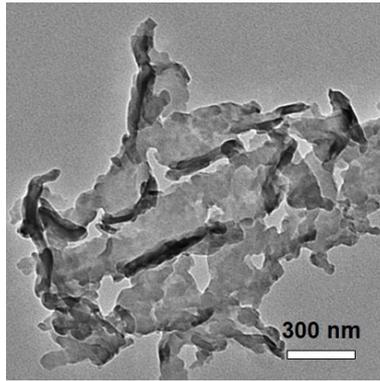
Figure S1. The representative TEM image of g-C$_3$N$_4$ nanosheet.
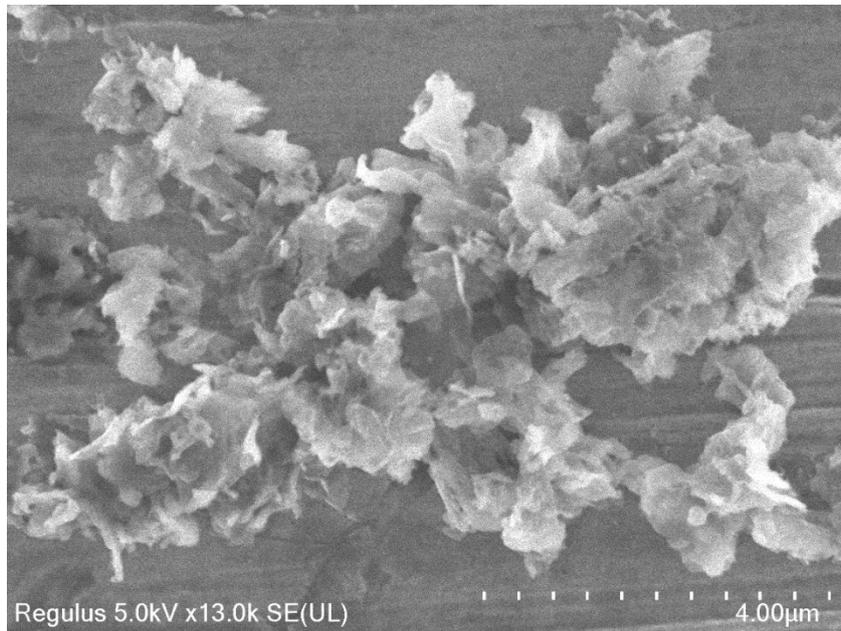
Figure S2. The representative SEM image of Au$_1$/g-C$_3$N$_4$ nanosheet.
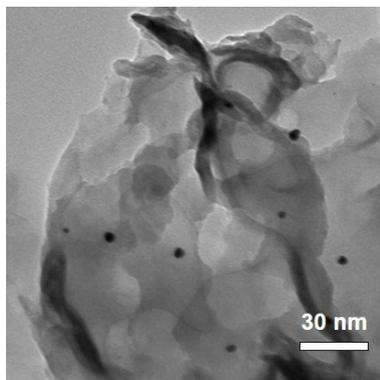
Figure S3. The representative TEM image of Au/g-C_3N_4 obtained at 130 °C.
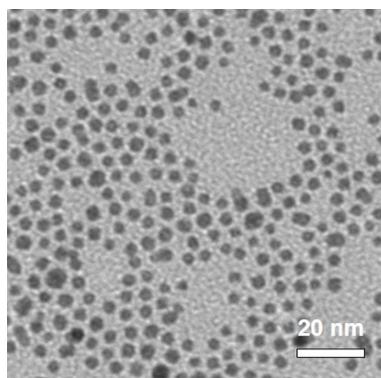
Figure S4. The representative TEM image of Au nanoparticles
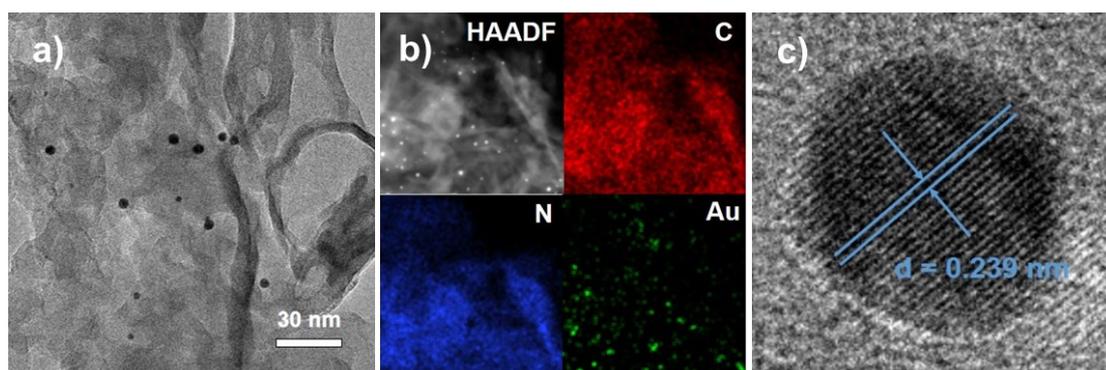
Figure S5. a) The representative TEM image of Au NPs/g-C_3N_4 through loading Au nanoparticles on g-C_3N_4 nanosheets and calcined at 400 °C in air; b) Energy dispersive spectroscopy mapping of Au NPs/g-C_3N_4 nanosheet; c) Interfringe distance measured by a single Au nanoparticle
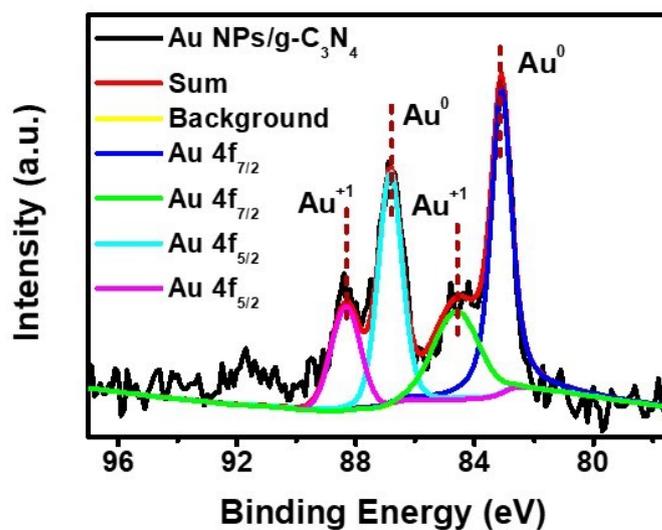
Figure S6. The Au 4f spectra of Au NPs/g-C$_3$N$_4$ nanosheet.
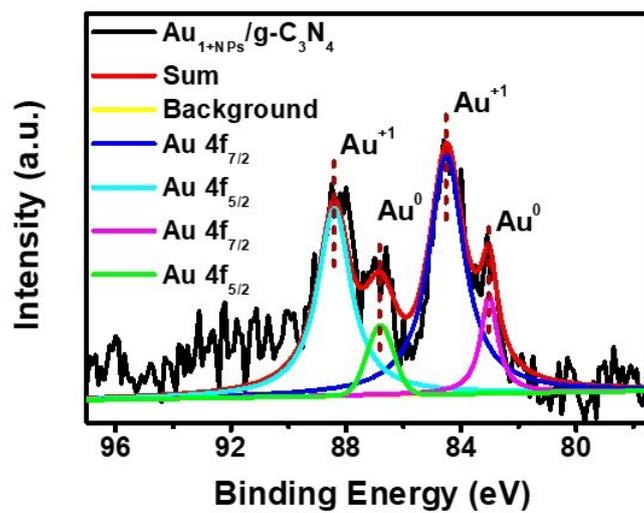
Figure S7. The Au 4f spectra of Au NPs/g-C$_3$N$_4$-130 obtained at 130 ^{o}C.
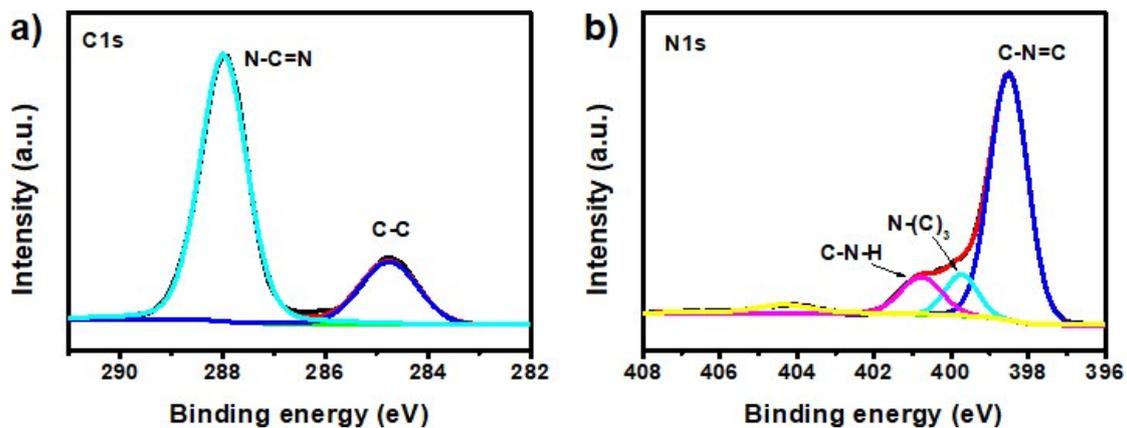
Figure S8. The C1s spectra (a) and N1s spectra (b) of Au_1/g-C_3N_4 nanosheet.
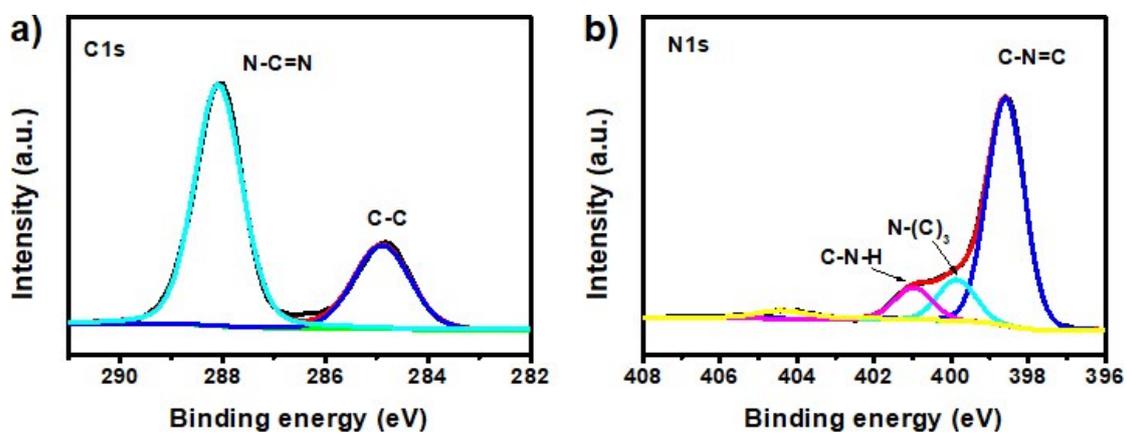
Figure S9. The C1s spectra (a) and N1s spectra (b) of Au NPs/g-C_3N_4 nanosheet.
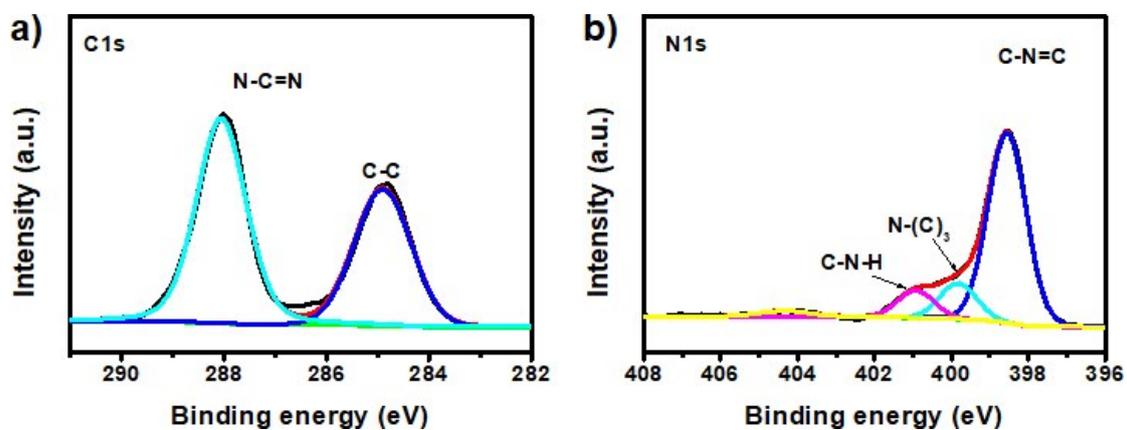
Figure S10. The C1s spectra (a) and N1s spectra (b) of Au NPs/g-C_3N_4-130 nanosheet.

References

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Analytical data for vinylsilanes

(*E*)-Triethyl(styryl)silane (**3aa**). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 19.2 Hz, 1H), 6.55 (d, *J* = 19.2 Hz, 1H), 1.11 (t, *J* = 7.8 Hz, 9H), 0.79 (q, *J* = 8 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 144.91, 138.59, 128.54, 127.93, 126.37, 125.95, 7.46, 3.59.

(E)-Triethyl(4-methylstyryl)silane (**3ba**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 19.2 Hz, 1H), 6.41 (d, *J* = 19.2 Hz, 1H), 2.37 (s, 3H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.69, 137.76, 135.87, 129.20, 126.24, 124.55, 21.23, 7.44, 3.56.

(E)-Triethyl(3-methylstyryl)silane (**3ca**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34-7.26 (m, 3H), 7.13 (d, *J* = 6.8 Hz, 1H), 6.95 (d, *J* = 19.2 Hz, 1H), 6.48 (d, *J* = 19.2 Hz, 1H), 2.42 (s, 3H), 1.06 (t, *J* = 8.0 Hz, 9H), 0.74 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 145.00, 138.52, 138.07, 128.72, 128.45, 127.04, 125.63, 123.57, 21.43, 7.46, 3.58.

(E)-Triethyl(4-methoxystyryl)silane (**3da**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8..4 Hz, 2H), 6.87 (d, J = 19.2 Hz, 1H), 6.30 (d, J = 19.2 Hz, 1H), 3.85 (s, 3H), 1.04 (t, J = 7.8 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 159.54, 144.24, 131.60, 127.56, 123.02, 113.90, 55.32, 7.47, 3.62.

(E)-3-(2-(triethylsilyl)vinyl)aniline (**3ea**). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.16 (t, J = 7.7 Hz, 1H), 6.91-6.82 (m, J = 23.7, 13.4 Hz, 3H), 6.63 (dd, J = 7.9 Hz, 1H), 6.41 (d, J = 19.3 Hz, 1H), 3.64 (s, 2H), 1.03 (t, J = 7.9 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 146.60, 144.99, 139.67, 129.43, 125.64, 117.17, 114.93, 112.75, 7.44, 3.57.

(*E*)-triethyl(4-(trifluoromethyl)styryl)silane (**3fa**). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 19.3 Hz, 1H), 6.57 (d, *J* = 19.3 Hz, 1H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.28, 141.76, 129.74, 126.46, 125.44, 7.36, 3.41.

(E)-triethyl(2-fluorostyryl)silane (**3ga**). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (dt, *J* = 8.6, 5.5 Hz, 1H), 7.28-7.22 (m, *J* = 8.7 Hz, 1H), 7.18-7.03 (m, *J* = 19.3 Hz, 3H), 6.52 (d, *J* = 19.3 Hz, 1H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.42, 158.94, 136.47, 129.14, 126.68, 124.00, 115.80, 115.58, 7.39, 3.48.

(E)-(4-chlorostyryl)triethylsilane (**3ha**). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 19.3 Hz, 1H), 6.45 (d, J = 19.3 Hz, 1H), 1.03 (t, J = 7.9 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 143.49, 137.03, 133.54, 128.66, 127.54, 126.95, 7.42, 3.52.

(E)-Triethyl(2-(naphthalene-2-yl)vinyl)silane (**3ia**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.86-7.80 (d, *J* = 8.4 Hz, 4H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.51-7.47 (m, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 18.4 Hz, 1H), 6.61 (d, *J* = 18.8 Hz, 1H), 1.07 (t, *J* = 8.0 Hz, 9H), 0.76 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 144.91, 136.02, 133.69, 133.33, 128.21, 128.15, 127.71, 126.58, 126.51, 126.25, 125.96, 123.37, 7.52, 3.64.

(E)-(4-Phenylbutyl-1-enyl)triethylsilane (**3ja**). ^{1}H NMR (400 MHz, CDCl3): δ 7.33-7.28 (m, 2H), 7.16-7.22 (m, 3H), 6.14 (dt, *J* = 18.8, 6.4 Hz, 1H), 5.62 (d, *J* = 18.8 Hz, 1H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.51-2.45 (m, 2H), 0.96 (t, *J* = 8.0 Hz, 9H), 0.60 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 147.49, 142.02, 128.51, 128.39, 128.35, 128.27, 126.59, 125.75, 38.82, 35.41, 7.40, 3.54.

(E)-Triethyl(hex-1-enyl)silane (**3ka**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.05 (dt, J = 18.8, 6.4 Hz, 1H), 5.55 (d, J = 18.8 Hz, 1H), 2.16-2.11 (m, 2H), 1.34- 1.28 (m, 4H), 1.00-0.89 (m, 12H), 0.56 (q, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 148.84, 125.48, 37.03, 31.37, 22.53, 14.06, 7.37, 3.56.

(E)-Triethyl(decyl-1-enyl)silane (**3la**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.04 (dt, J = 18.8, 6.4 Hz, 1H), 5.56 (d, J = 18.8 Hz, 1H), 2.15-2.06 (m, 2H), 1.46-1.28 (m, 12H), 0.99-0.87 (m, 12H), 0.56 (q, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 148.84, 125.48, 37.08, 31.91, 29.48, 29.31, 28.85, 22.70, 14.09, 7.35, 3.57.

(E)-(5-Chloropent-1-enyl)triethylsilane (**3ma**). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.99 (dt, J = 18.8, 6.4 Hz, 1H), 5.62 (d, J = 18.8 Hz, 1H), 3.53 (t, J = 6.6 Hz, 2H), 2.31-2.24 (m, 2H), 1.91-1.81 (m, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.54 (q, J = 8.0 Hz, 6H); ^{13}C NMR (101 MHz, CDCl$_3$): δ 146.15, 127.65, 44.42, 33.96, 31.61, 7.37, 3.46.

¹H NMR peaks: 7.34, 7.31, 7.30, 7.28, 7.26, 7.14, 7.12, 6.97, 6.92, 6.50, 6.46, 2.42, 1.08, 1.06, 1.04, 0.76, 0.74, 0.72, 0.70

Integrations: 3.07, 0.99, 1.00, 0.93, 3.15, 9.15, 6.13

¹³C NMR peaks: 145.00, 138.52, 138.07, 128.72, 128.45, 127.04, 125.63, 123.57, 21.43, 7.46, 3.58

^1H NMR spectrum

7.18, 7.16, 7.14, 6.91, 6.89, 6.83, 6.82, 6.64, 6.62, 6.61, 6.44, 6.39, 3.64, 1.05, 1.03, 1.01, 0.73, 0.71, 0.69, 0.67

1.00, 3.04, 0.99, 0.97, 1.99, 9.35, 6.33

^{13}C NMR spectrum

146.60, 144.99, 139.67, 129.43, 125.64, 117.17, 114.93, 112.75, 7.44, 3.57

7.59 7.57 7.54 7.52 6.94 6.90 6.59 6.54   1.02 1.00 0.98 0.72 0.70 0.68 0.66

2.24 2.18   1.00   1.00   9.18   6.21

f1 (ppm)

143.28 141.76   129.74 126.46 125.44   77.34 77.02 76.70   7.36 3.41

f1 (ppm)

¹H NMR peaks: 7.62, 7.62, 7.60, 7.60, 7.58, 7.58, 7.27, 7.27, 7.26, 7.25, 7.24, 7.24, 7.23, 7.22, 7.18, 7.16, 7.14, 7.13, 7.12, 7.08, 7.06, 7.04, 7.03, 6.55, 6.50

1.05, 1.03, 1.01, 0.74, 0.72, 0.70, 0.68

Integrations: 1.02, 1.14, 2.12, 1.18, 1.00, 9.34, 6.36

¹³C NMR peaks: 161.42, 158.94, 136.47, 129.14, 126.68, 124.00, 115.80, 115.58, 7.39, 3.48

7.42 7.39 7.34 7.32   6.91 6.86   6.47 6.43

1.05 1.03 1.02   0.74 0.72 0.70 0.68

2.06 2.06   1.00   1.01

9.08   6.43

143.49 137.03 133.54 128.66 127.54 126.95

7.42 3.52

1H NMR peaks: 7.87, 7.86, 7.84, 7.82, 7.75, 7.74, 7.50, 7.49, 7.49, 7.48, 7.13, 7.12, 7.10, 6.63, 6.59, 1.09, 1.07, 1.06, 0.79, 0.77, 0.75, 0.73

Integrations: 2.13, 2.14, 1.05, 2.28, 1.00, 1.00

13C NMR peaks: 144.91, 136.02, 133.69, 133.33, 128.21, 128.15, 127.71, 126.58, 126.51, 126.25, 125.96, 123.37, 7.52, 3.64

¹H NMR spectrum (top) with peaks at 7.33, 7.31, 7.30, 7.28, 7.26, 7.23, 7.22, 6.16, 6.15, 6.13, 6.11, 6.10, 6.08, 5.65, 5.60, 2.78, 2.76, 2.74, 2.51, 2.49, 2.47, 2.45, 0.98, 0.96, 0.94, 0.62, 0.60, 0.58, 0.56 ppm. Integrations: 5.29, 1.00, 1.00, 2.47, 2.26, 9.33, 6.19.

¹³C NMR spectrum (bottom) with peaks at 147.49, 142.02, 128.51, 128.39, 128.35, 128.27, 126.59, 125.75, 38.82, 35.41, 7.40, 3.54 ppm.

1H NMR peaks:
6.02, 6.01, 5.99, 5.98, 5.96, 5.95, 5.64, 5.59, 3.55, 3.53, 3.51, 2.31, 2.30, 2.28, 2.26, 2.24, 1.91, 1.90, 1.88, 1.86, 1.84, 1.83, 1.81, 0.94, 0.92, 0.90, 0.57, 0.55, 0.53, 0.51

Integrations: 1.01, 1.00, 2.01, 2.31, 2.09, 8.93, 6.43

f1 (ppm)

13C NMR peaks:
146.15, 127.65, 44.42, 33.96, 31.61, 7.37, 3.46

f1 (ppm)