Supporting Information

1 Experimental Techniques

1.1 SCHLENK Technique

Manipulations of air- and/or moisture-sensitive compounds were conducted under an inert gas atmosphere. Glassware was therefore dried in a drying cabinet at 120°C prior to use. For use, the glassware was connected to a vacuum system. Traces of air and moisture were removed by alternate evacuation and influx of inert gas. Additionally, MBRAUN gloveboxes were used for handling and storage of air sensitive compounds.

1.2 Vacuum System

The vacuum system used consists of a dual manifold with several ports. While one manifold was connected to a source of inert gas, the other was connected to a slide vane rotary vacuum pump of the brand VACUUBRAND. To protect the vacuum pump from contamination by solvent vapors as well as gaseous reaction products, two liquid nitrogen cooling traps are interposed between line and pump. An ultimate vacuum of $1 \cdot 10^{-3}$ mbar was achieved.

1.3 Drying of the Solvents Used

The solvents *n*-pentane, *n*-heptane, toluene and diethylether were dried using a SPS-800 solvent purification system of the company MBRAUN and used after collection without additional drying steps. The drying of *n*-hexane and tetrahydrofuran and dichloromethane was carried out by heating under reflux over sodium or potassium and P_4O_{10}, respectively, and subsequent distillation.

The dried solvents were stored in SCHLENK flasks under inert gas.

1.4 Measuring Instruments and Methods of Measurement

1.4.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

The NMR spectra were recorded on a BRUKER *Advance 300* (300 MHz ^{1}H NMR or 75 MHz. ^{13}C NMR), a BRUKER *Advance 400* (400 MHz ^{1}H NMR or 101 MHz ^{13}C NMR) or a Bruker *Ascend 400* (400 MHZ ^{1}H NMR). For sample preparation, 5-10 mg of the substance were solved in 0.4-0.5 mL of a deuterated solvent ($CDCl_3$, 99.8 atom% D; C_6D_6, 99.6 atom% D) in a NMR tube having a diameter of 5 mm. For the measurement of air- and/or moisture-sensitive samples, dried deuterated solvents and YOUNG NMR tubes or NMR tubes with screw caps were used. Alternatively, NMR tubes were sealed by melting in the presence of a flame. The chemical shift (δ) was given in ‘parts per million’ (ppm) using tetramethylsilane (TMS, $\delta = 0.00$ ppm) as reference compound for ^{1}H, and ^{13}C experiments. For ^{31}P experiments, chemical shifts were referenced to 85% phosphoric acid ($\delta = 0.00$ ppm). Referencing of the spectra was carried out using the signal of the not fully deuterated solvents. The following reference values were used:

$CDCl_3$-d_1:	^{1}H NMR: $\delta = 7.260$ ppm	^{13}C NMR: $\delta = 77.160$ ppm
C_6D_6-d_6:	^{1}H NMR: $\delta = 7.160$ ppm	^{13}C NMR: $\delta = 128.06$ ppm
THF-d_8	^{1}H NMR: $\delta = 3.580$ ppm	^{13}C NMR: $\delta = 67.570$ ppm

The coupling constant J was given in Hertz (Hz). For the signal patterns occurring in the NMR spectra, following abbreviations were used: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet) and m (multiplet).

^{1}H, ^{13}C and ^{31}P spectra are cropped to a range that shows all signals and allows good readability.

1.4.2 Infrared (IR) Spectroscopy

Infrared spectra were recorded on a BRUKER *Tensor 37*. During the recording of the background spectra as well as during the actual measurement the measuring chamber was flushed by a constant nitrogen flow. The signal strength was given using the following assignments: vs (very strong), s (strong), w (weak), vw (very weak).

1.4.3 Size exclusion chromatography

SEC data was collected in order to determine the molecular weight distribution of the synthesized polymers as well as to prove the decrease of the hydrodynamic volume after the intramolecular collapse of the metallopolymer chains in to the respective SCNPs. The SEC analyses were carried out on a *PL-SEC 50 Plus Integrated System* by Varian and Polymer Laboratories running on tetrahydrofuran (THF; HPLC-grade). The columns applied were a *PLgel Mixed C* guard column (50 × 7.5 mm), followed by three *PLgel Mixed C* linear columns (300 × 7.5 mm, 5 μm beadsize) and a differential refractive index (RI) detector. The device was operated at 35 °C column temperature with a flow rate of 1 mL·min-1. The columns were calibrated using linear polystyrene standards ranging from 476 to 2.5 x 106 g·mol-1. For the measurement, the samples were dissolved in THF (2 mg·mL-1) and filtered through PTFE membranes with a pore size of 0.2 μm prior to injection. To obtain Mn and Đ values, the integration of the polymer peak was carried out from low elution times to approximately 40 minutes due to overlap with an SEC system peak. No baseline correction was performed. Consequently, Mn and Đ values are estimates

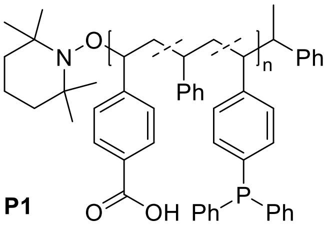
1.4.4 Dynamic Light Scattering (DLS)

The DLS measurements were carried out on a Nicomp 380 DLS spectrometer from Particle Sizing Systems, Santa Barbara, USA (laser diode: 90 mW, 658 nm). The polymer solutions were prepared by dissolving the polymer samples in chloroform or THF at a concentration of 6 mg mL-1 for both, linear polymers and SCNPs. Before being analyzed, the solutions were filtered over a 0.2 μL filter. The measurements were performed in automatic mode at 25 °C and evaluated by a standard Gaussian and 3 an advanced evaluation method, the latter using an inverse Laplace algorithm that allows to analyze multimodal distributions (NICOMP). Normally, the threshold is set to 3 %, if not otherwise indicated. Numbers given in text are the number weighted average values as calculated by the NICOMP evaluation. All measurements were determined at 90° to the incident beam.

2 Synthesis Procedures

2.1 Polymer Synthesis

P1 – Poly(styrol-co-4-(diphenylphosphino)styrol-co-4-(vinyl-benzoesäure) (P1)



P1

In a vial, 2,2,6,6-tetramethyl-1-(1-phenylethoxy)-piperidine (13.8 mg, 0.05 mmol, 1.0 eq.), styrene (4.67 mL, 4.25 g, 40.8 mmol, 760 eq.), 4-vinylbenzoic acid (159 mg, 1.07 mmol, 20 eq.) and diphenyl(4-vinylphenyl)phosphine (309 mg, 1.07 mmol, 20 eq.) were dissolved in 1.5 mL DMF. The solution was purged with argon for 1 h and subsequently stirred at 125°C for 6 h. By allowing the mixture to cool to ambient temperature and allowing air contact, the polymerization was quenched. The reaction mixture was diluted with 10 mL DCM and precipitated in cold MeOH. The solid was filtered, dissolved in DCM and again precipitated in cold MeOH. This procedure was repeated one more time. After filtration and drying of the solid in high vacuum, the product was obtained as colorless powder (2.07 g).

SEC (THF, RI): M_n = 38 500 g·mol^{-1}, M_p = 43 500 g·mol^{-1}, $Đ$ = 1.1.

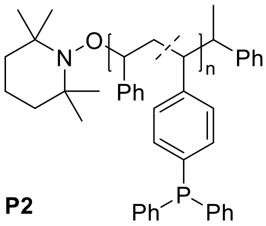
^{1}H NMR (400 MHz, THF-d_8): δ [ppm] = 11.2 (bs, COOH), 7.97-7.55 (m, aromatic protons in *ortho*-position of 4-vinylbenzoic acid), 7.55-7.20 (m, aromatic protons of diphenyl(4-vinylphenyl)phosphine, 7.20-6.25 (m, aromatic protons of styrene and 4-vinylbenzoic acid), 2.37-1.06 (m, aliphatic protons).

By ^{1}H NMR spectroscopy a monomer ratio of 36:1 (styrene:diphenyl(4-vinylphenyl)-phosphine) was determined, consequently, 3% of phosphine-units are contained in the polymer chains (0.27 mmol per 1.00 g of polymer). Similarly, a ratio of 16:1 was determined for styrene:4-vinylbenzoic acid. There are approx. 6% of benzoic acid units incorporated in the polymer chain or 0.57 mmol per 1.00 g of polymer. Based on these values the number of functional groups were calculated as follows: By having a molecular mass for styrene of 104.15 g·mol^{-1} and a molecular mass for the polymer of 38 500 g·mol^{-1}, 22 benzoic acid units and 11 phosphine units are estimated per polymer chain.

$^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8): δ [ppm] = −6.28 (s, PPh_2Ar).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083 (w), 3059 (m), 3026 (s), 2924 (s), 2849 (m), 1734 (m), 1692 (m), 1602 (m), 1578 (vw), 1491 (s), 1451 (s), 1369 (vw), 1312 (vw), 1284 (vw), 1178 (vw), 1090 (vw), 1025 (w), 761 (s), 749 (m), 698 (vs), 539 (m), 501 (w).

P2 – Poly(styrol-co-4-(diphenylphosphino)styrol)



P2

In a photo vial 10.1 mg 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)-piperidine (0.04 mmol, 1.0 eq.), 4.06 mL styrene (3.70 mg, 35.6 mmol, 920 eq.) and 442 mg diphenyl(4-vinylphenyl)phosphine (1.53 mmol, 40 eq.) were dissolved in 1 mL DMF. The reaction solution was purged with argon for 1 h and subsequently stirred at 125°C for 5 h. By allowing the mixture to cool to ambient temperature and allowing air contact, the polymerization was quenched. The reaction mixture was diluted with 10 mL DCM and precipitated in cold MeOH. The solid was filtered, dissolved in DCM and again precipitated in cold MeOH. This procedure was repeated one more time. After filtration and drying of the solid in high vacuum, the product was obtained as colorless powder (1.58 g).

SEC (THF, RI): M_n = 34 000 g·mol^{-1}, M_p = 40 500 g·mol^{-1}, $Đ$ = 1.2.

^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.41-7.19 (m, aromatic protons of diphenyl(4-vinylphenyl)phosphine), 7.19-6.21 (m, aromatic protons of styrene) 2.45-1.07 (m, aliphatic protons).

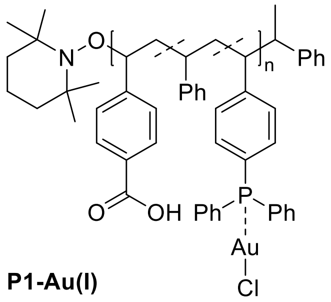
By ^1H NMR spectroscopy a monomer ratio of 20:1 (styrene: diphenyl(4-vinylphenyl)-phosphine) was determined. Consequently, 5% phosphine moieties were incorporated in the polymer chains (0.51 mmol per 1.00 g of polymer).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ [ppm] = 29.1 (s, $O{=}PPh_2Ar$, less than 5%), -6.21 (s, PPh_2Ar).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083 (w), 3059 (m), 3025 (s), 3000 (vw), 2923 (s), 2849 (m), 1601 (m), 1491 (s), 1450 (s), 1370 (vw), 1182 (vw), 1154 (vw), 1092 (vw), 1068 (vw), 1026 (w), 907 (vw), 824 (vw), 762 (vw), 746 (s), 697 (vs), 540 (m), 503 (w).

2.2 Metallopolymer Synthesis

P1-Au(I) starting from P1



P1-Au(I)

17.5 g chloro(tetrahydrothiophene)gold(I) (0.05 mmol, 1.00 eq.) and 200 mg poly(styrene-*co*-diphenyl(4-vinylphenyl)phosphine-*co*-4-vinylbenzoic acid (**P1**) (200 mg, 0.05 mmol phosphine units, 1.00 eq.) were dissolved in 10 mL dry DCM and stirred for 1 h at ambient temperature in the absence of light. Subsequently, the reaction mixture was concentrated and precipitated by dropwise addition into cold MeOH. The solid was filtered and dried in high vacuum. **P1-Au(I)** was obtained as colorless powder (186 mg).

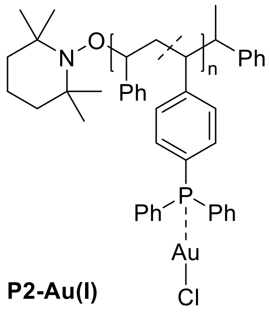
SEC (THF, RI): M_n = 39 000 g·mol^{-1}, M_p = 46 000 g·mol^{-1}, $Đ$ = 1.2.

^{1}H NMR (400 MHz, THF-d_8): δ [ppm] = 11.0 (bs, COO*H*), 7.97-7.60 (m, aromatic protons in *ortho*-position of 4-vinylbenzoic acid), 7.60-7.34 (m, aromatic protons of diphenyl(4-vinylphenyl)phosphine), 7.34-6.20 (m, aromatic protons of styrene and 4-vinylbenzoic acid), 2.38-1.15 (m, aliphatic protons).

^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ [ppm] = 31.6 (s, ClAu-*P*Ph$_2$Ar).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083 (m), 3059 (s), 3025 (w), 2923 (s), 2849 (m), 1943 (vw), 1869 (vw), 1798 (vw), 1734 (m), 1695 (m), 1652 (w), 1602 (m), 1540 (vw), 1493 (s), 1451 (s), 1313 (w), 1284 (w), 1180 (w), 1155 (vw), 1103 (w), 1068 (vw), 1027 (w), 965 (w), 907 (vw), 844 (vw), 750 (s), 697 (vs), 624 (vw), 540 (m).

P2-Au(I) starting from P2



P2-Au(I)

48.5 mg Chloro(tetrahydrothiophene)gold(I) (0.150 mmol, 1.00 eq.) and 300 mg poly(styrol-*co*-4-(diphenylphosphino)styrol) (**P2**) (0.150 mmol phosphine units, 1.00 eq.) were dissolved in 10 mL dry DCM and stirred for 1 h at ambient temperature in the absence of light. Subsequently, the reaction mixture was concentrated and precipitated by dropwise addition into cold MeOH. The solid was filtered and dried in high vacuum. **P2-Au(I)** was obtained as colorless powder (330 mg).

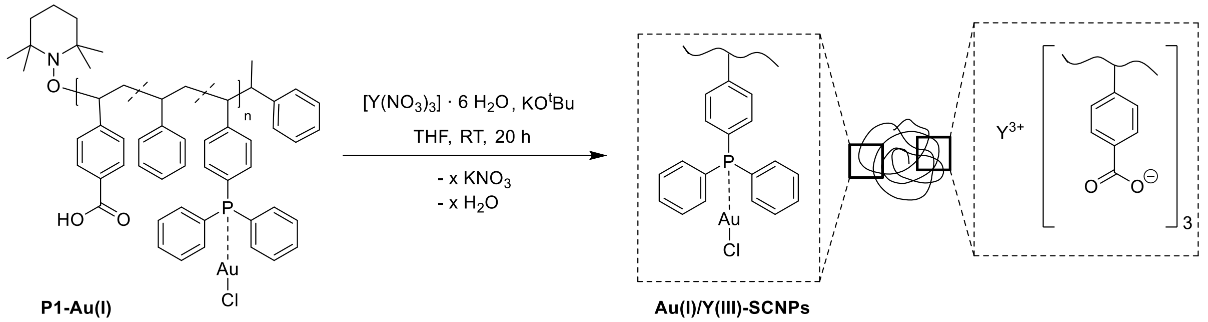
SEC (THF, RI): M_n = 35 000 g·mol^{-1}, M_p = 45 000 g·mol^{-1}, $Đ$ = 1.2.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.68-7.33 (m, aromatic protons of diphenyl(4-vinylphenyl)phosphine), 7.33-6.17 (m, aromatic protons of styrene), 2.27-1.07 (m, aliphatic protons).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ [ppm] = 32.4 (s, ClAu-*P*Ph_2Ar).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3082 (w), 3058 (m), 3025 (s), 2999 (vw), 2923 (s), 2849 (m), 1600 (m), 1491 (s), 1452 (s), 1405 (w), 1370 (w), 1309 (vw), 1183 (w), 1155 (vw), 1102 (m), 1068 (w), 1026 (m), 907 (vw), 825 (w), 749 (s), 696 (vs), 540 (m) 509 (w).

2.3 Synthesis of the Au(I)/Y(III)-SCNPs



In a 200 mL round bottom flask 3.66 mg yttrium(III)nitrate (9.56 µmol, 0.33 eq.) and 3.51 mg potassium *tert*-butoxide (28.7 µmol, 1.0 eq.) were dissolved in 150 mL dry THF. Subsequently, a solution of 50.0 mg **P1-Au(I)** (28.7 µmol benzoic acid units, 1.0 eq.) in 20 mL dry THF was added dropwise using a syringe pump (drip rate: 1 mL · h^{-1}). After complete addition of the metallopolymer the solution was concentrated to a volume of 1-2 mL and precipitated by dropwise addition into cold MeOH. The solid was filtered and dried in high vacuum. The product was obtained as colorless solid (35 mg).

SEC (THF, RI): M_n = 29 500 g·mol^{-1}, M_p = 36 000 g·mol^{-1}, $Đ$ = 1.2.

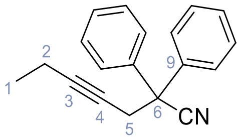
^{1}H NMR (400 MHz, THF-*d$_8$*): δ [ppm] = 7.87-7.60 (m, aromatic protons in *ortho*-position of 4-vinylbenzoic acid), 7.60-7.35 (m, aromatic protons of diphenyl(4-vinylphenyl)phosphine), 7.35-6.01 (m, aromatic protons of styrene and 4-vinylbezoic acid), 2.39-1.00 (m, aliphatic protons).

$^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8): δ [ppm] = 32.4 (s, ClAu-*P*Ph$_2$Ar).

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3083 (w), 3059 (m), 3026 (s), 3000 (vw), 2925 (s), 2849 (m), 1942 (vw), 1803 (vw), 1602 (m), 1557 (vw), 1514 (w), 1492 (s), 1452 (s), 1417 (m), 1377 (m), 1184 (w), 1155 (vw), 1103 (w), 1069 (vw), 1026 (w), 907 (vw), 842 (w), 751 (s), 698 (vs), 541 (m).

2.4 Synthesis of the Substrates

Precursor of 1-Ph – 2,2-Diphenylhept-4-ynenitrile



$C_{19}H_{17}N$
M = 259,35

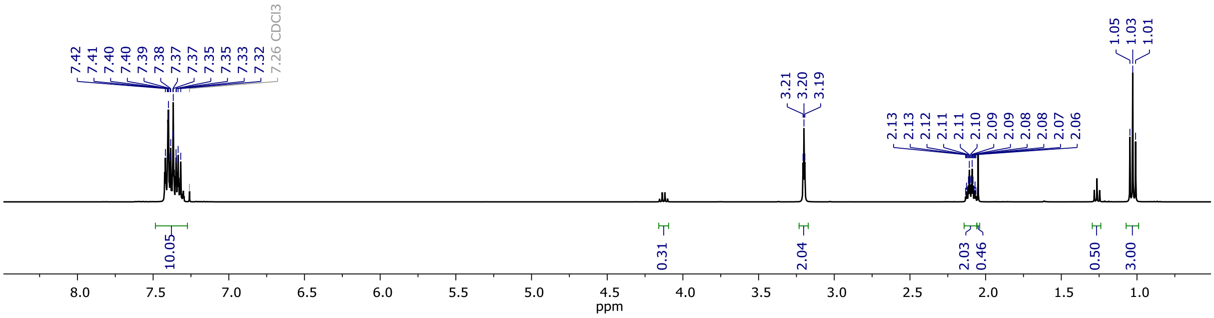
The synthesis of the precursor of **1-Ph** was carried out following a modification of the literature known procedure.[1]

0.745 g NaH (31.1 mmol, 1.2 eq.) were dissolved in 10 mL dry THF. At 0°C a solution of 5.00 g diphenylacetonitrile (25.9 mmol, 1.0 eq.) in 30 mL dry THF was added dropwise. The resulting solution was warmed to ambient temperature and stirred for 30 min. Subsequently, the reaction mixture was cooled to 0°C again and 1-bromo-2-pentyne was added. After complete addition, the mixture was warmed to ambient temperature and stirred for 14 h. The reaction mixture was poured into 90 mL of an ice/water-mixture, extracted with diethylether (3 × 60 mL), dried over Na_2SO_4 and concentrated in vacuum. The crude product was subjected to column chromatography (Petroleum ether/EtOAc 50:1 (v/v), $R_f = 0.30$). The product was obtained as colorless oil (6.05 g, 23.2 mmol, 90%).

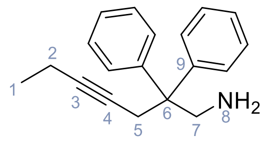
^1H NMR (400 MHz, C_6D_6-d_6): δ [ppm] = δ 7.59 – 7.16 (m, 10 H, H_{Ph}), 3.20 (t, J = 2.4 Hz, 2 H, H5), 2.10 (qt, J = 7.5, 2.4 Hz, 2 H, H2), 1.03 (t, J = 7.5 Hz, 3 H, H1).

---

[1] J. Luo, Q. Cao, X. Cao, X. Zhao, *Nat. Commun*. **2018**, *9*, 527.



1-Ph – 2,2-Diphenylhept-4-yn-1-amine



1-Ph

$C_{19}H_{21}N$
M = 263.38 g/mol

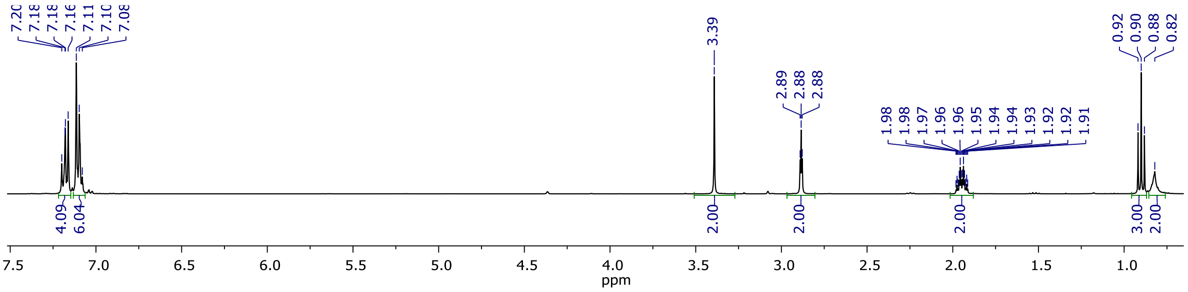
The synthesis of compound **1-Ph** was carried out following a slight modification of the literature known procedure.[2]

6.00 g of the precursor (23.1 mmol, 1.0 eq.) were dissolved in 100 mL dry Et_2O and slowly added dropwise to a suspension of 3.51 g $LiAlH_4$ (92.5 mmol, 4.0 eq.) in 100 mL dry Et_2O at 0°C. The resulting reaction mixture was warmed to ambient temperature and stirred for 22 h or until the reaction was complete (monitored *via* TLC). The reaction was cooled to 0°C and carefully quenched with cold water, warmed to ambient temperature, and stirred for 15 min. Subsequently, 100 mL 10% NaOH are added and the mixture was stirred for 15 min. Afterwards, the aqueous phase was extracted with Et_2O (3 × 200 mL). The combined organic layers were washed with brine (2 × 150 mL), dried over Na_2SO_4 and dried in high vacuum. The resulting oil was degassed. The product **1-Ph** was obtained as slightly yellow oil (5.53 g, 21.0 mmol, 91%).

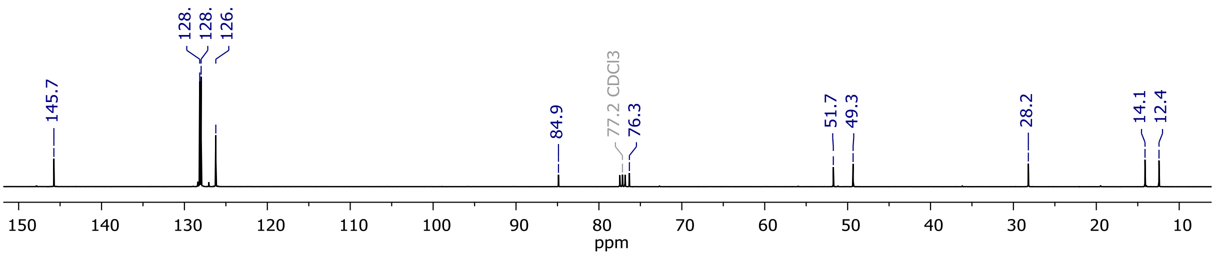
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.23 – 7.14 (m, 4 H, *m*-CH_{Ph}), 7.13 – 7.06 (m, 6 H, *o*-CH_{Ph} and *p*-CH_{Ph}), 3.39 (s, 2 H, H7), 2.88 (t, J = 2.4 Hz, 2 H, H5), 1.95 (qt, J = 7.5, 2.4 Hz, 2 H, H2), 0.90 (t, J = 7.5 Hz, 3 H, H1), 0.82 (s, 2 H, NH).

---

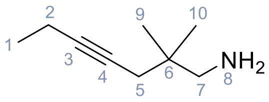
[2] J. Luo, Q. Cao, X. Cao, X. Zhao, *Nat. Commun*. **2018**, *9*, 527.



^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 145.8 (C9), 128.2 (C_{Ph}), 128.0 (C_{Ph}), 126.2 (C_{Ph}), 84.9 (C3), 76.3 (C4), 51.7 (C6), 49.3 (C7), 28.2 (C5), 14.1 (C1), 12.4 (C2).



1-Me – 2,2-Dimethylhept-4-yn-1-amine



1-Me

$C_9H_{17}N$
M = 139,24

The synthesis of compound **1-Me** was carried out following a slight modification of the literature known procedure.[3]

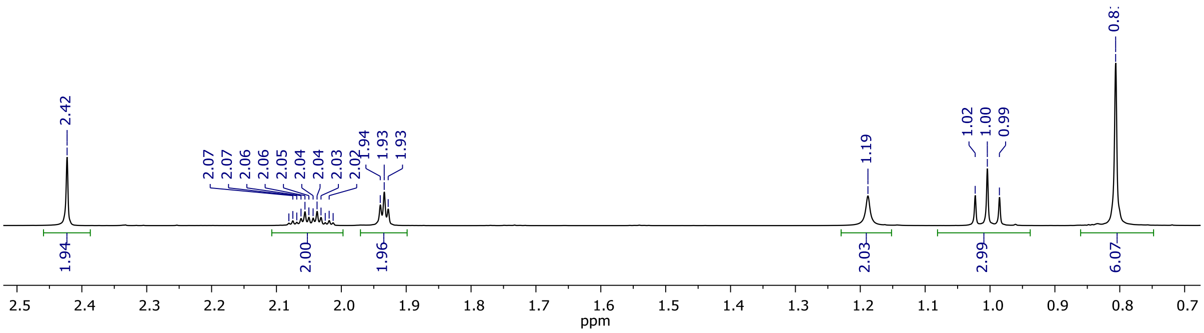
9.20 mL diisopropylamine (6.60 g, 65.2 mmol, 1.0 eq.) were dissolved in 200 mL THF and cooled to −78°C. 26.2 mL of *n*-Butyllithium (2.5 M in hexane, 65.3 mmol, 1.0 eq.) were added with stirring. After 15 min, the mixture was warmed to 0°C and 5.80 mL isobutyronitrile (4.47 g, 64.7 mmol, 1.0 eq.) were slowly added dropwise. The reaction mixture was stirred for 2 h. Subsequently, 6.70 mL of 1-bromopent-2-yne (9.63 g, 65.5 mmol, 1.0 eq.) were added dropwise. After stirring at 0°C for 16 h, the solvent was removed under reduced pressure and the remaining oil was purified *via* distillation (164°C oil bath temperature, 6 mbar, no VIGREUX column). The intermediate product was obtained as colorless liquid (8.40 g, 62.1 mmol, 95%).

---

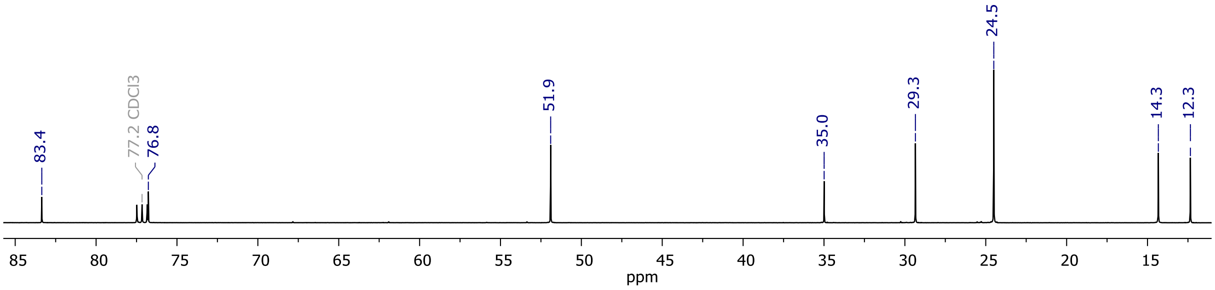
[3] M.Oishi, Y. Nakanishi, H. Suzuki, *Inorg. Chem.* **2017**, *56*, 9802-9813.

For the second step, 4.00 g of the intermediate (29.6 mmol, 1.0 eq.) were dropwise added to a suspension of 1.70 g $LiAlH_4$ (44.8 mmol, 1.5 eq.) in 200 mL Et_2O. The reaction mixture was refluxed for 2 h. The mixture was cooled in an ice bath and quenched with 10 mL THF/water-mixture and 10 mL 15% NaOH. The precipitate was filtered and washed with THF. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The remaining oil was redissolved in CH_2Cl_2 and filtered with a PTFE syringe filter. The solvent was removed under reduced pressure. The product **1-Me** was obtained as slightly yellow viscose oil (2.40 g, 17.2 mmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.42 (s, 2H, H7), 2.05 (qt, J = 7.5, 2.4 Hz, 2H, H2), 1.93 (t, J = 2.4 Hz, 2H, H5), 1.19 (s, 2H, NH), 1.00 (t, J = 7.5 Hz, 3H, H1), 0.81 (s, 6H, H9,10).



^{13}C NMR (101 MHz, $CDCl_3$): δ [ppm] = 83.4 (C3), 76.8 (C4), 51.9 (C7), 35.0 (C6), 29.4 (C5), 24.5 (C9,10), 14.3 (C1), 12.4 (C2).



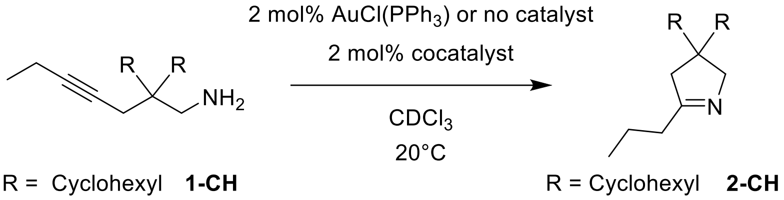
The analytical data matches the values reported in literature.[4]

---

[4] M.Oishi, Y. Nakanishi, H. Suzuki, *Inorg. Chem.* **2017**, *56*, 9802-9813.

3 Catalysis

3.1 Investigation of potential cocatalysts



The cocatalyst used in the hydroamination catalyses should not show any catalytic activity itself, to not distort the catalytic activities determined for the actual catalysts used. Therefore, [AgNTf$_2$], [TlOTf], [Zn(OTf)$_2$] and [NaBArF] were tested as potential catalysts in blind tests. For the blind tests, 2 mol% of the respective cocatalyst were dissolved in CDCl$_3$ and the substrate **1-CH** was added. With [AgNTf$_2$] a conversion of **1-CH** to **2-CH** of 93% after 17 h was obtained, ruling out this silver salt as potential cocatalyst. All other compounds showed very low conversion rates (Table S1). Afterwards, the compounds were used together with the commercially available gold catalyst [AuClPPh$_3$], to determine whether they are able to effectively activate the catalyst. Therefore, the respective potential cocatalysts was solved in CDCl$_3$ together with [AuClPPh$_3$] and stirred for 15 min at room temperature. Subsequently, the substrate **1-CH** was added and the conversion was determined by ^{1}H NMR spectroscopy (Table S1).

Table S1: Determination of suitable cocatalysts for the activation of the catalysts used in the intramolecular hydroamination of aminoalkynes. The commercial catalyst [AuCl(PPh$_3$)] was used as benchmark system, **1-CH** as exemplary substrate. The reactions were conducted in CDCl$_3$ and the conversion determined by ^{1}H NMR spectroscopy (similar as for the catalyses performed later, for more information, see below).

#	cocatalyst (2 mol%)	Gold(I) Catalyst (2 mol%)	time [h]	conversion [%]
1	[AgNTf$_2$]	[AuCl(PPh$_3$)]	17	96
2	[AgNTf$_2$]	—	17	93
3	[TlOTf]	[AuCl(PPh$_3$)]	20	quant.
4	[TlOTf]	—	20	< 1
5	[Zn(OTf)$_2$]	[AuCl(PPh$_3$)]	16	quant.
6	[Zn(OTf)$_2$]	—	16	2
7	[NaBArF]	[AuCl(PPh$_3$)]	20	96
8	[NaBArF]	—	20	6
9	—	[AuCl(PPh$_3$)]	24	5

All compounds could activate the catalyst $[AuCl(PPh_3)]$, resulting in almost quantitative conversion of **1-CH** to **2-CH**. Furthermore, it was shown that the activation of the catalyst is essential to reach high conversion rates (Table S1 entry 9).

As Tl(I) compounds are highly toxic and Zn(II) ions show some affinity towards carboxylic acids and could therefore potentially coordinate towards the benzoic acid units contained in the **Au(I)/Y(III)-SCNPs** and the benchmark system **P2-Au(I)**, $NaBAr^F$ was chosen as cocatalysts for all catalyses conducted.

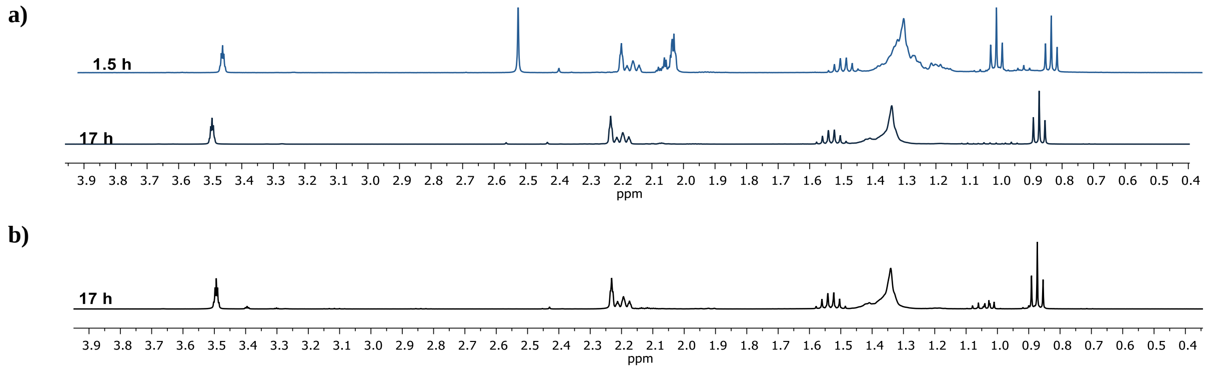


Figure S1: a) ^{1}H NMR spectra for the conversion of **1-CH** to **2-CH** with just $[AgNTf_2]$ (no gold(I) catalyst, "blind test"; Table S1 entry 2). After 17 h a conversion of 93% was reached. b) ^{1}H NMR spectrum for the conversion of **1-CH** to **2-CH** with $[AuClPPh_3]$ as gold catalyst and $[AgNTf_2]$ as cocatalyst (Table S1 entry 1). After 17 h a conversion of 96% was reached. For sake of the clearness, only the part of the spectra used for integration is displayed.

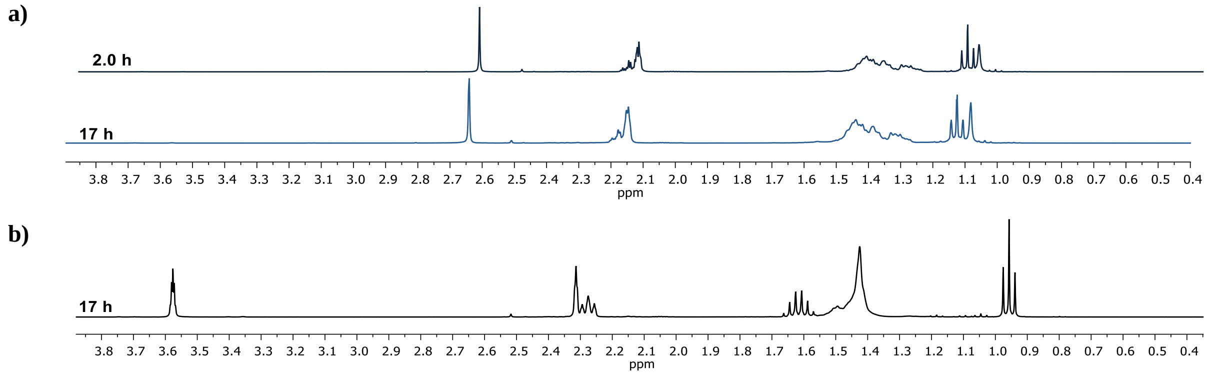


Figure S2: ^{1}H NMR spectra for the conversion of **1-CH** to **2-CH** with just [TlOTf] (no gold(I) catalyst, "blind test"; Table S1 entry 2). After 20 h a conversion of <1% was reached. b) ^{1}H NMR spectrum for the conversion of **1-CH** to **2-CH** with $[AuClPPh_3]$ as gold catalyst and [TlOTf] as cocatalyst (Table S1 entry 1). After 20 h a conversion of 100% was reached. For sake of the clearness, only the part of the spectra used for integration is displayed.

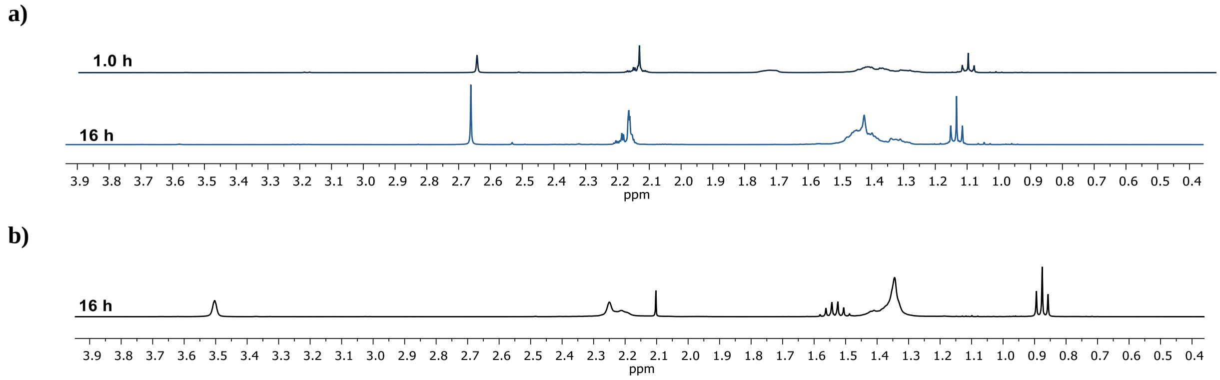


Figure S3: ^{1}H NMR spectra for the conversion of **1-CH** to **2-CH** with just [Zn(OTf)$_2$] (no gold(I) catalyst, “blind test”; Table S1 entry 2). After 16 h a conversion of 2% was reached. b) ^{1}H NMR spectrum for the conversion of **1-CH** to **2-CH** with [AuClPPh$_3$] as gold catalyst and [Zn(OTf$_2$)] as cocatalyst (Table S1 entry 1). After 16 h a conversion of 100% was reached. For sake of the clearness, only the part of the spectra used for integration is displayed.

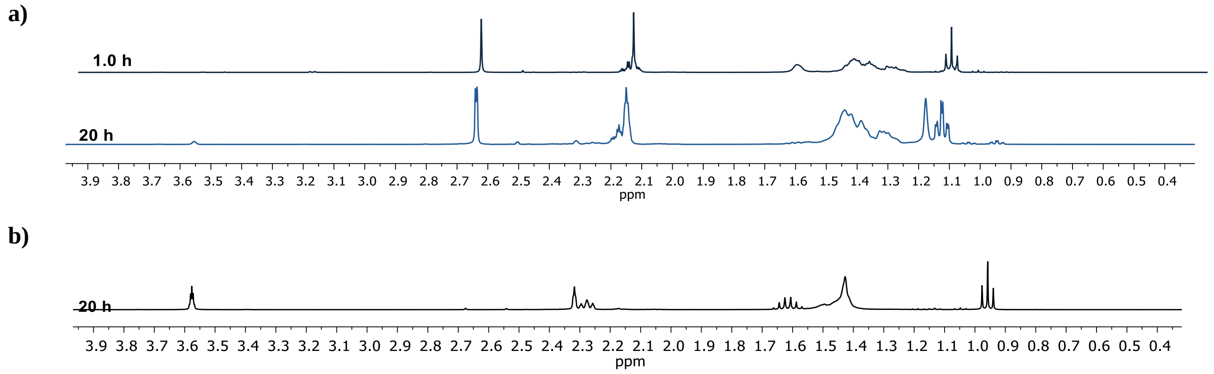
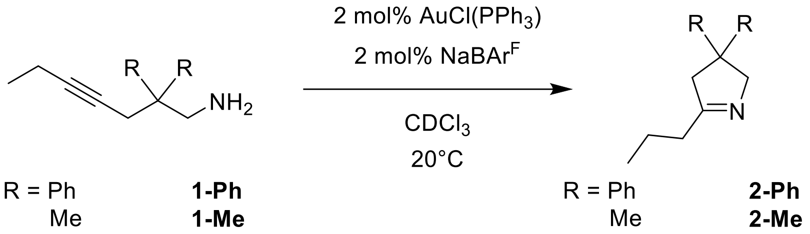


Figure S4: ^{1}H NMR spectra for the conversion of **1-CH** to **2-CH** with just [NaBAr^F] (no gold(I) catalyst, “blind test”; Table S1 entry 2). After 20 h a conversion of 6% was reached. b) ^{1}H NMR spectrum for the conversion of **1-CH** to **2-CH** with [AuClPPh$_3$] as gold catalyst and [NaBAr^F] as cocatalyst (Table S1 entry 1). After 20 h a conversion of 96% was reached. For sake of the clearness, only the part of the spectra used for integration is displayed.

3.2 Intramolecular Hydroamination: [AuCl(PPh3)] as Catalyst



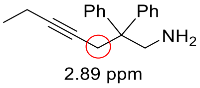
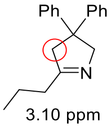
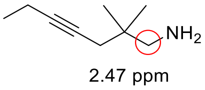
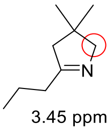
In a YOUNG NMR tube [AuCl(PPh$_3$)] (0.02 eq.), NaBAr^F (0.02 eq.) and ferrocene (0.1 eq.) were dissolved in CDCl$_3$ and stirred for 30 min at ambient temperature. Subsequently, the mixture is frozen with liquid nitrogen, the substrate (**1-Ph** or **1-Me**; 1.0 eq.) is added and frozen using liquid nitrogen. The mixture was thawed right before insertion into the core of the NMR machine (= t$_0$). To monitor the conversion, ^{1}H NMR spectra were recorded at t = 0 h, 1 h, 2 h, 4 h, 6 h, 10 h, 24 h and 48 h. The sample temperature was thereby kept between 20 and 25°C. The conversion was determined *via* comparison of the integrals of characteristic signals of starting material and product, using ferrocene as internal reference:

$$Conversion\ [\%] = \left(\frac{I_{Product}}{I_{Starting\ Material} + I_{Product}}\right) \cdot 100$$

The amount of CDCl$_3$ used was adapted for each catalysis, so that the concentration of the catalyst was $0.0026\ \frac{mmol}{mL}$.

The exact weights of sample taken as well as the ^{1}H NMR signals used can be seen in the following table.

Table S2: Overview of the exact weights of sample taken as well as the ^{1}H NMR signals used for the calculation of the conversion for each catalysis carried out. Protons marked in the structures were used for the determination of the conversion, the numbers given are the chemical shifts of these (in $CDCl_3$, recorded on a 400 MHz spectrometer).

#	Substrate	Resonance Starting Material[5]	Resonance Product[1]	Weight of sample taken	Conversion after 24h
1	1-Ph			Substrate: 0.067 g (0.254 mmol, 1.0 eq.) [AuCl(PPh3)]: 0.0019 g (0.004 mmol, 0.02 eq.) NaBAr^F: 0.003 g (0.003 mmol, 0.02 eq.) Ferrocene: 0.004 g (0.019 mmol, 0.08 eq.)	100%
2	1-Me			Substrate: 0.022 g (0.158 mmol, 1.0 eq.) [AuCl(PPh3)]: 0.0013 g (0.003 mmol, 0.02 eq.) NaBAr^F: 0.002 g (0.003 mmol, 0.02 eq.) Ferrocene: 0.002 g (0.013 mmol, 0.08 eq.)	87%

---

[5] The ppm value displayed next to the structures gives the chemical shift of the signal of the protons that was used for the calculation of the conversion. The respective protons are marked with a red circle.

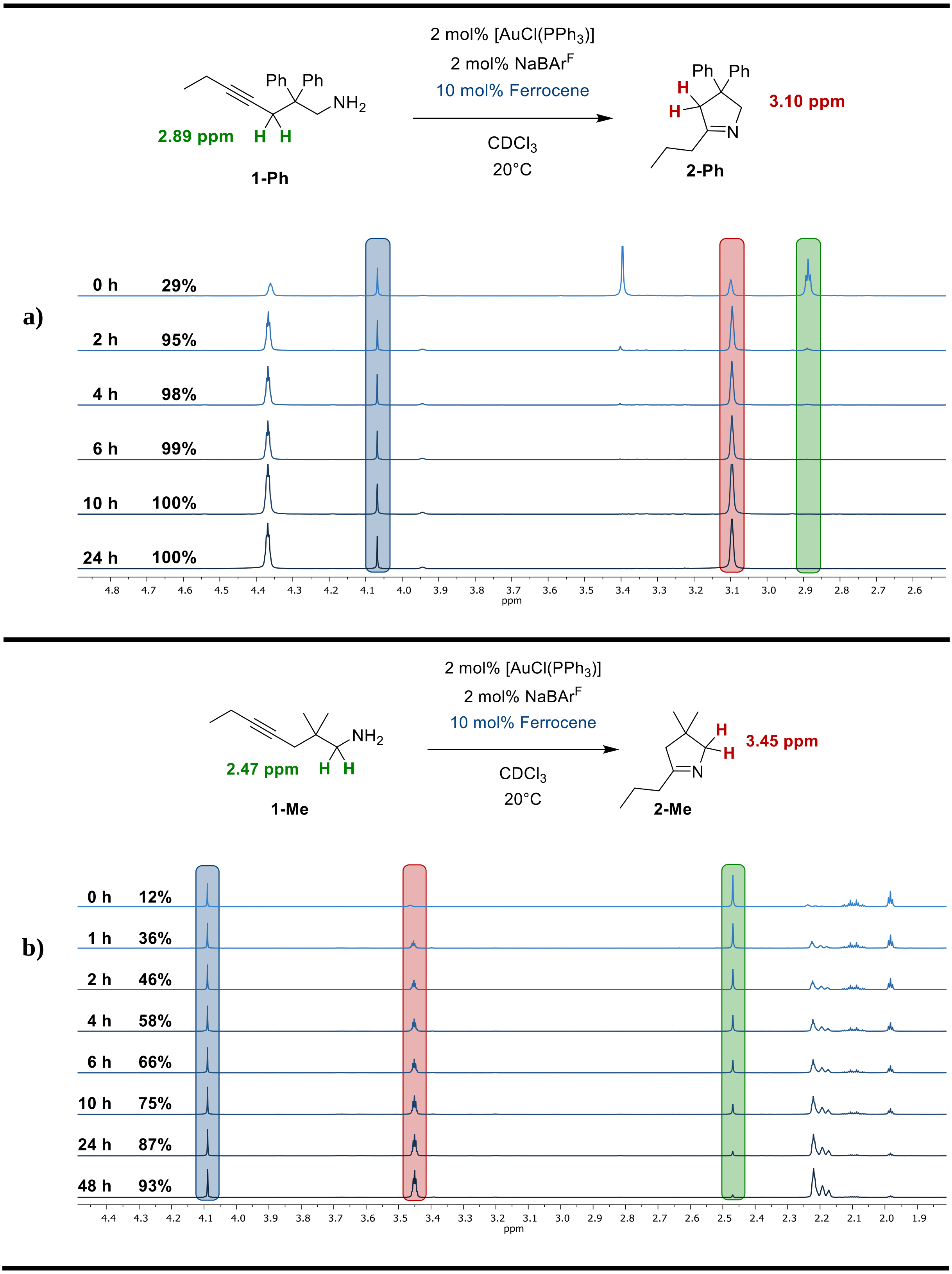
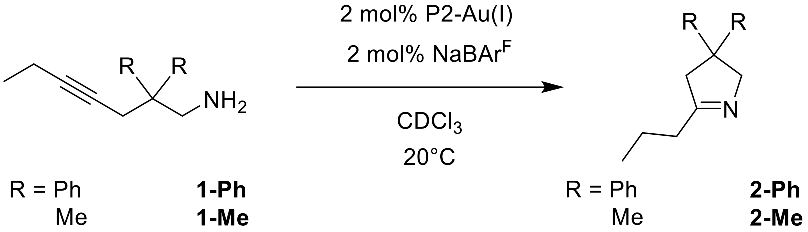
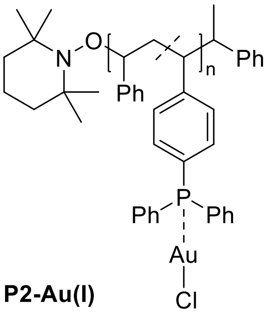


Figure S5: Reaction equations and ^{1}H NMR spectra of selected points in time with the respective conversions for the [AuCl(PPh$_3$)] **68** catalyzed hydroaminations. The protons used for integration and their corresponding NMR signals were marked in green for the substrate and in red for the product, respectively. The intensity of the spectra was normalized using the ferrocene signal (4.08 ppm). For sake of the clearness, only the part of the spectra used for integration is displayed. **a)** Hydroamination of substrate **1-Ph**. **b)** Hydroamination of substrate **1-Me**. ^{1}H NMR spectra of selected points in time are displayed.

3.3 Intramolecular Hydroamination: P2-Au(I) as Catalyst



The intramolecular hydroaminations using **P2-Au(I)** as catalyst were carried out similar to the catalysis with [AuCl(PPh$_3$)] as catalyst (*cf.* 3.1).

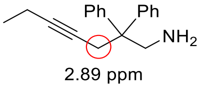
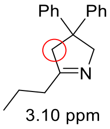
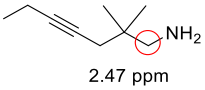
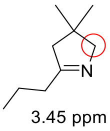


P2-Au(I)

Figure S6: Structure of the polymer catalyst P2-Au(I). 1.00 g polymer contains 0.505 mmol of AuCl-phosphine-moieties (calculated from the NMR spectra).

The exact weights of sample taken as well as the ^{1}H NMR signals used can be seen in the following table.

Table S3: Overview of the exact weights of sample taken as well as the ^{1}H NMR signals used for the calculation of the conversion for each catalysis carried out. Protons marked in the structures were used for the determination of the conversion, the numbers given are the chemical shifts of these (in $CDCl_3$, recorded on a 400MHz spectrometer).

#	Substrate	Resonance Starting Material[6]	Resonance Product[1]	Weight of sample taken	Conversion after 24h
1	1-Ph			Substrate: 0.050 g (0.190 mmol, 1.0 eq.) P2-Au(I): 0.0075 g (0.004 mmol, 0.02 eq.) NaBAr^{F}: 0.003 g (0.004 mmol, 0.02 eq.) Ferrocene: 0.004 g (0.019 mmol, 0.1 eq.)	100%
2	1-Me			Substrate: 0.020 g (0.144 mmol, 1.0 eq.) P2-Au(I): 0.0051 g (0.003 mmol, 0.02 eq.) NaBAr^{F}: 0.002 g (0.003 mmol, 0.02 eq.) Ferrocene: 0.002 g (0.013 mmol, 0.09 eq.)	98%

---

[6] The ppm value displayed next to the structures gives the chemical shift of the signal of the protons that was used for the calculation of the conversion. The respective protons are marked with a red circle.

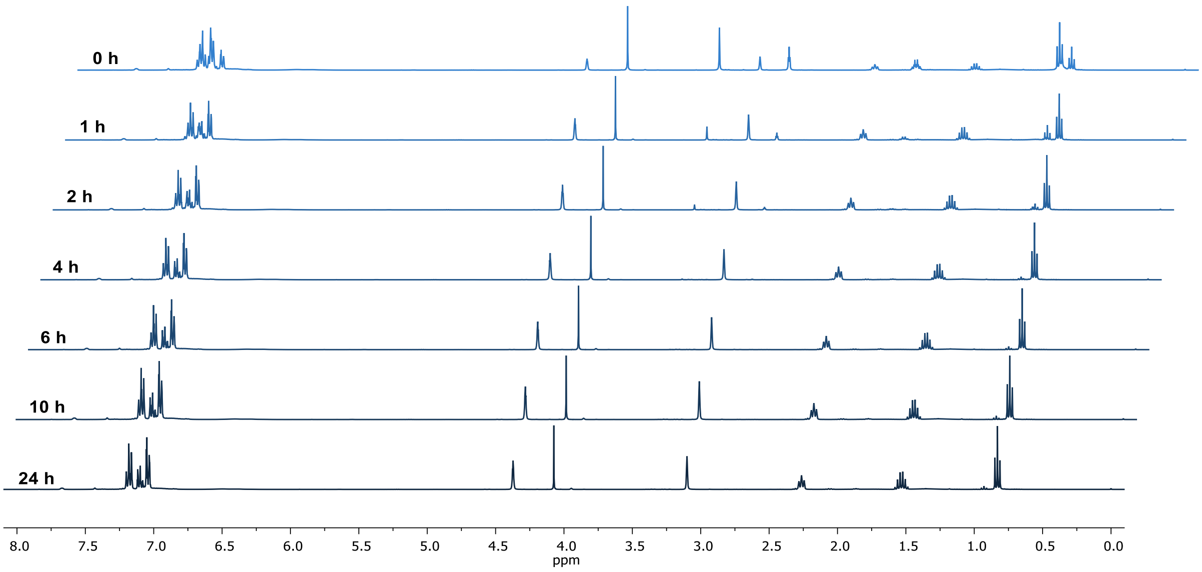


Figure S7: ^{1}H NMR spectra of the hydroamination of **1-Ph** catalyzed by **P2-Au(I)**.

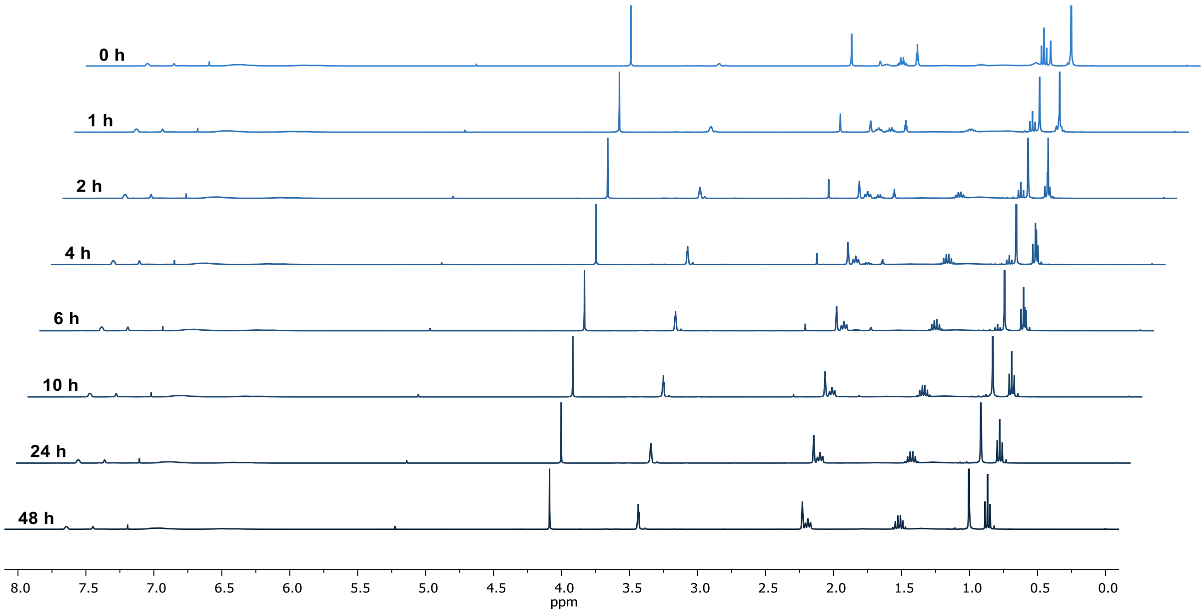
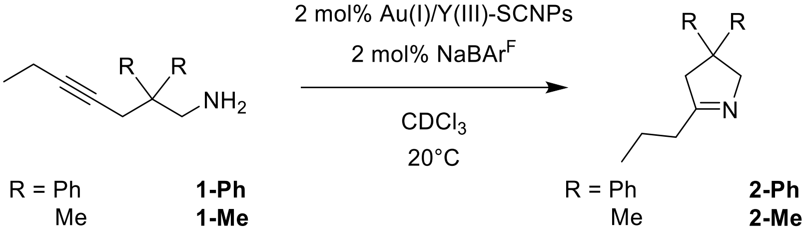


Figure S8: ^{1}H NMR spectra of the hydroamination of **1-Me** catalyzed by **P2-Au(I)**.

3.4 Intramolecular Hydroamination: Au(I)/Y(III)-SCNPs as Catalyst



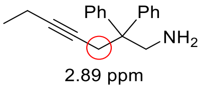
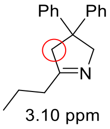
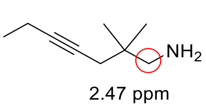
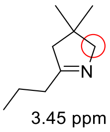
The **Au(I)/Y(III)-SCNPs** (0.02 eq.) were dissolved in $CDCl_3$ over night or until fully dissolved. The catalyst solution was added to $NaBAr^F$ (0.02 eq.) and ferrocene (0.1 eq.) in a YOUNG NMR tube and stirred for 30 min at ambient temperature. Subsequently, the mixture was frozen with liquid nitrogen, the substrate (**1-Ph** or **1-Me**; 1.0 eq.) was added and frozen using liquid nitrogen. The mixture was thawed right before insertion into the core of the NMR machine (= t_0). To monitor the conversion, ^{1}H NMR spectra were recorded at t =0 h, 1 h, 2 h, 4 h, 6 h, 10 h, 24 h and 48 h. The sample temperature was thereby kept between 20 and 25°C. The conversion was determined *via* comparison of the integrals of characteristic signals of starting material and product, using ferrocene as internal reference:

$$Conversion\ [\%] = \left(\frac{I_{Product}}{I_{Starting\ Material} + I_{Product}}\right) \cdot 100$$

1.00 g Au(I)/Y(III)-SCNPs contains 0.270 mmol of AuCl-phosphine moieties (calculated from the NMR spectra).

The exact weights of sample taken as well as the ^{1}H NMR signals used can be seen in the following table.

Table S4: Overview of the exact weights of sample taken as well as the ^{1}H NMR signals used for the calculation of the conversion for each catalysis carried out. Protons marked in the structures were used for the determination of the conversion, the numbers given are the chemical shifts of these (in $CDCl_3$, recorded on a 400MHz spectrometer).

#	Substrate	Signal Starting Material[7]	Signal Product[1]	Weight of sample taken	Conversion after 24h
1	1-Ph			Substrate: 0.050 g (0.190 mmol, 1.0 eq.) SCNPs: 0.0141 g (0.004 mmol, 0.02 eq.) NaBAr^F: 0.003 g (0.004 mmol, 0.02 eq.) Ferrocene: 0.004 g (0.019 mmol, 0.1 eq.)	100%
2				Substrate: 0.027 g (0.103 mmol, 1.0 eq.) SCNPs: 0.0070 g (0.002 mmol, 0.02 eq.) NaBAr^F: 0.002 g (0.002 mmol, 0.02 eq.) Ferrocene: 0.002 g (0.09 mmol, 0.09 eq.)	100%
3	1-Me			Substrate: 0.013 g (0.090 mmol, 1.0 eq.) SCNPs: 0.0066 g (0.002 mmol, 0.02 eq.) NaBAr^F: 0.002 g (0.002 mmol, 0.02 eq.) Ferrocene: 0.002 g (0.009 mmol, 0.1 eq.)	79%
4				Substrate: 0.013 g (0.090 mmol, 1.0 eq.) SCNPs: 0.0066 g (0.002 mmol, 0.02 eq.) NaBAr^F: 0.002 g (0.002 mmol, 0.02 eq.) Ferrocene: 0.002 g (0.009 mmol, 0.1 eq.)	77%

---

[7] The ppm value displayed next to the structures gives the chemical shift of the signal of the protons that was used for the calculation of the conversion. The respective protons are marked with a red circle.

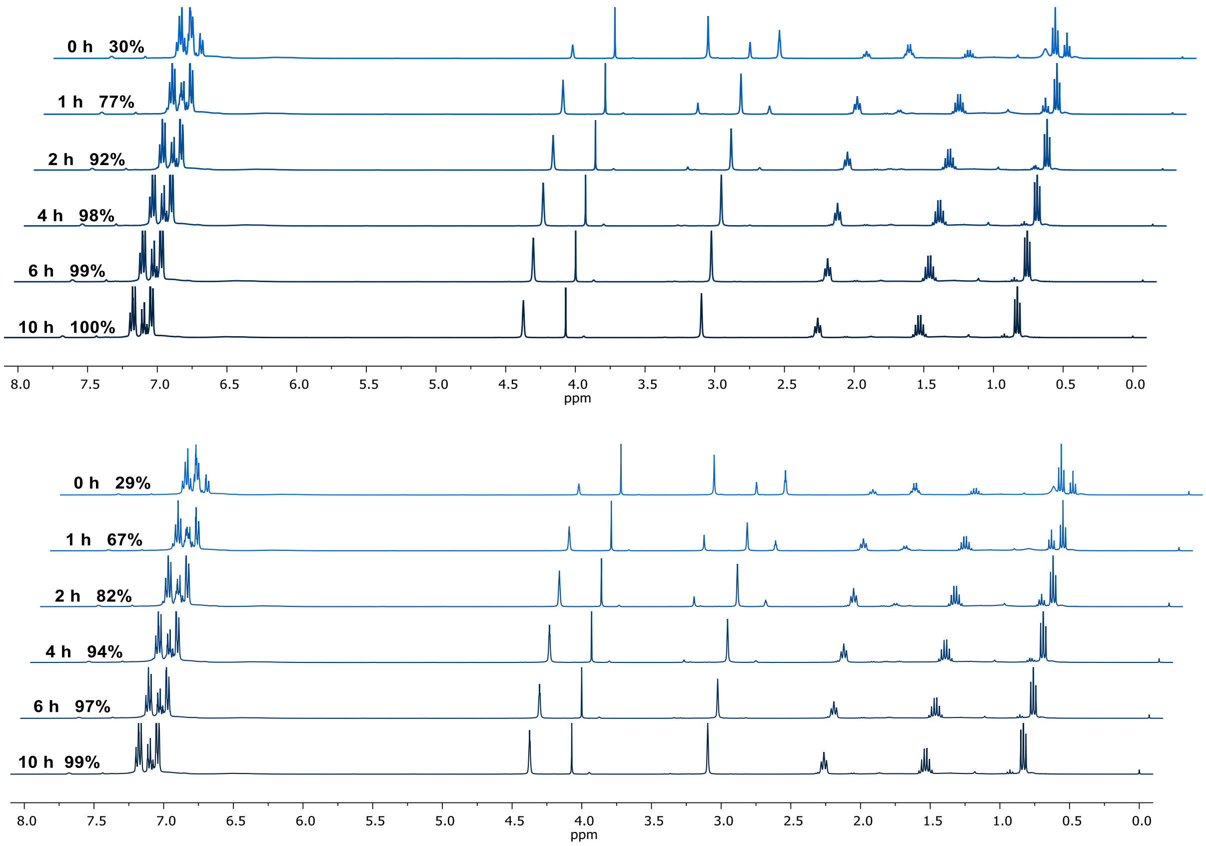


Figure S9: ^{1}H NMR spectra of the hydroamination of **1-Ph** catalyzed by **Au(I)/Y(III)-SCNP**s (see Table S4, entries 1 and 2).

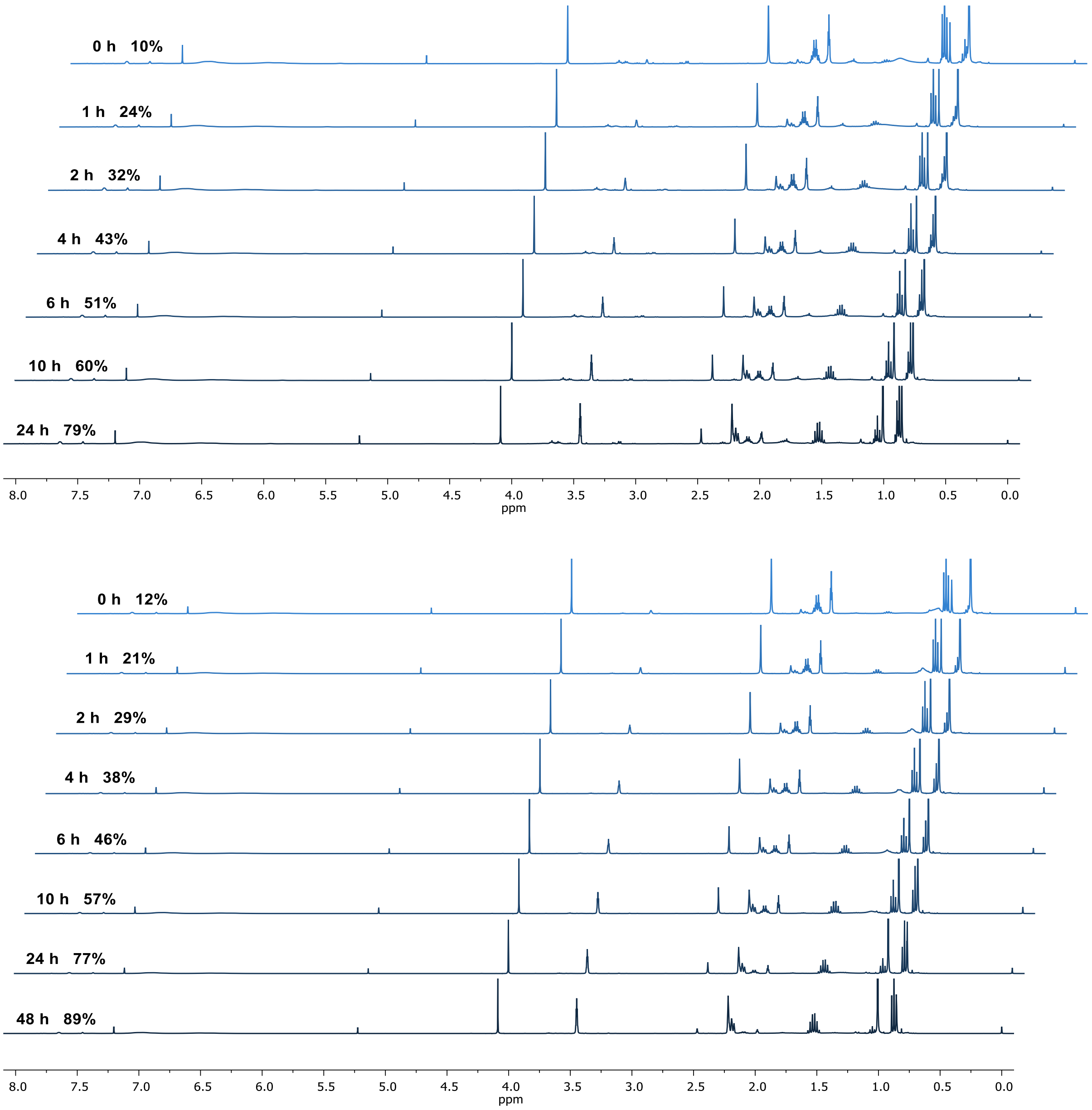
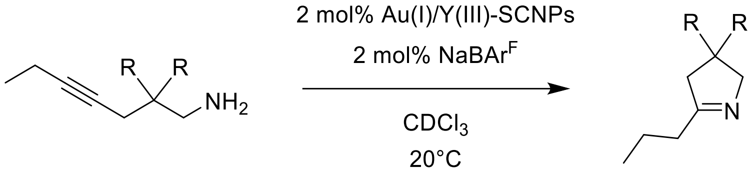


Figure S10: ^{1}H NMR spectra of the hydroamination of **1-Me** catalyzed by **Au(I)/Y(II**I)-SCNPs (see Table S4, entries 3 and 4).

3.5 Intramolecular Hydroamination: Recovery of the Au(I)/Y(III)-SCNPs and Renewed Catalysis with the Recovered Catalyst



R = Ph **1-Ph**
Me **1-Me**

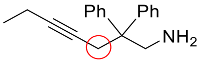
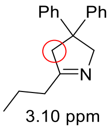
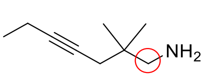
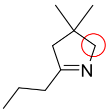
R = Ph **2-Ph**
Me **2-Me**

The Au(I)/Y(III)-SCNPs were precipitated from the reaction mixture by dropwise addition of the latter into dry methanol. The precipitate was filtered, washed with dry methanol, and dried in high vacuum. The recovered SCNPs were used again as catalyst for intramolecular hydroamination. The amount of catalyst recovered, and details of the catalysis is shown in the following tables.

Table S5: Catalysis from which the **Au(I)/Y(III)-SCNPs** were recovered and amount of recovered catalyst.

#	Recovered from	Amount recovered
1	Table 3.1, #1	72%
2	Table 3.1, #4	81%

Table S6: Overview of the exact weights of sample taken as well as the 1H NMR signals used for the calculation of the conversion for each catalysis carried out. Protons marked in the structures were used for the determination of the conversion, the numbers given are the chemical shifts of these (in CDCl3, recorded on a 400MHz spectrometer).

#	Substrate	Signal Starting Material[*]	Signal Product[1]	Weight of sample taken	Conversion after 24h
1	1-Ph	 2.89 ppm	 3.10 ppm	Substrate: 0.036 g (0.136 mmol, 1.0 eq.) SCNPs: 0.0101 g (0.003 mmol, 0.02 eq.) NaBAr^F: 0.002 g (0.003 mmol, 0.02 eq.) Ferrocene: 0.003 g (0.014 mmol, 0.1 eq.)	93%
2	1-Me	 2.47 ppm	 3.45 ppm	Substrate: 0.010 g (0.073 mmol, 1.0 eq.) SCNPs: 0.0054 g (0.001 mmol, 0.02 eq.) NaBAr^F: 0.001 g (0.001 mmol, 0.02 eq.) Ferrocene: 0.001 g (0.007 mmol, 0.1 eq.)	47%

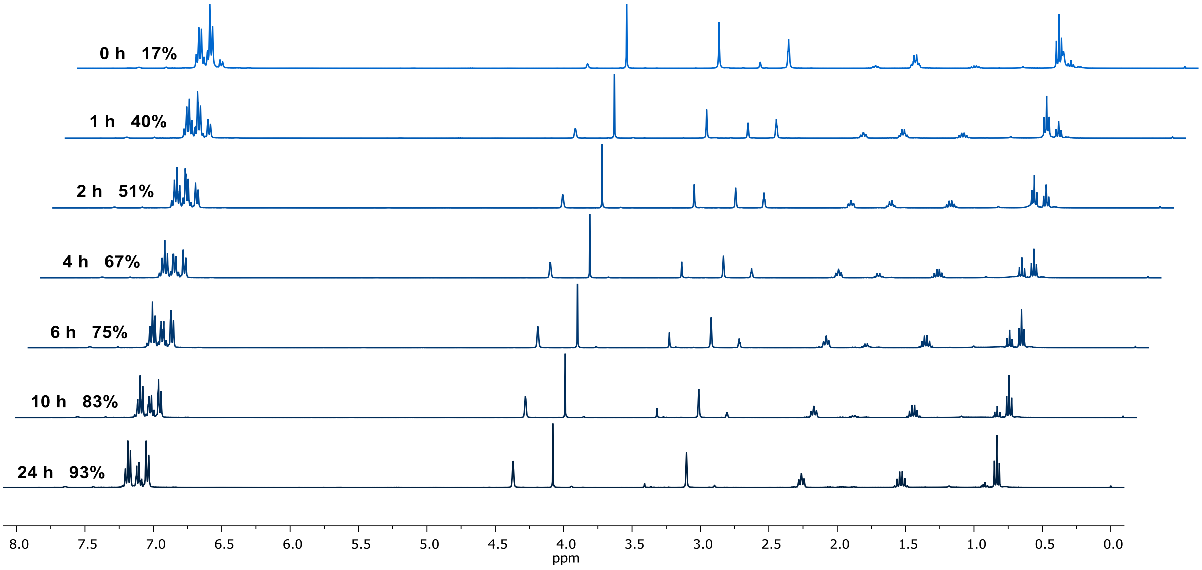


Figure S11: ^{1}H NMR of the hydroamination of **1-Ph** with recovered **Au(I)/Y(III)-SCNPs** (2nd catalytic cycle).

---

[*] The ppm value displayed next to the structures gives the chemical shift of the signal of the protons that was used for the calculation of the conversion. The respective protons are marked with a red circle.

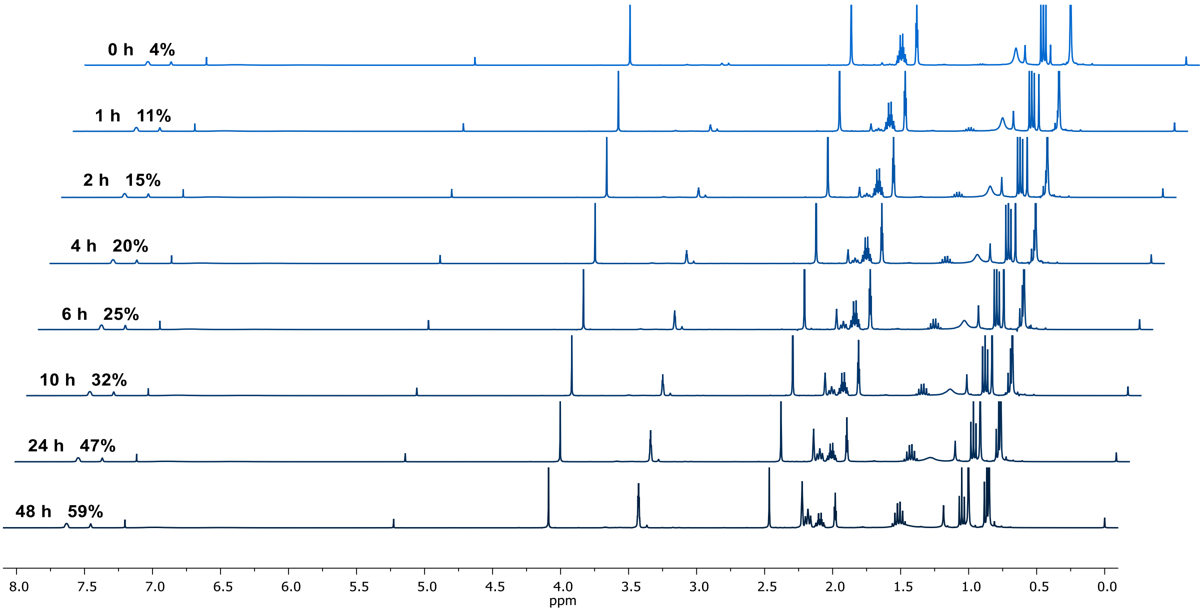
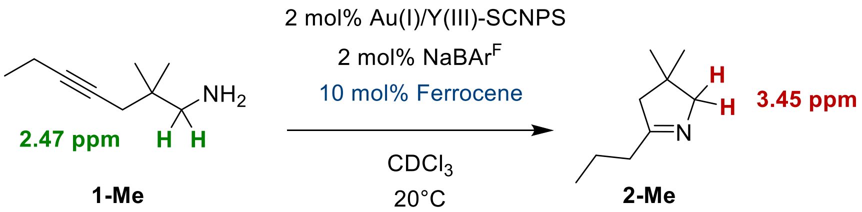


Figure S12: ^{1}H NMR of the hydroamination of **1-Me** with recovered **Au(I)/Y(III)-SCNP**s (2nd catalytic cycle).

3.6 Kinetic Investigations

For the investigation of the kinetics of the catalysis, the reaction order was determined experimentally.



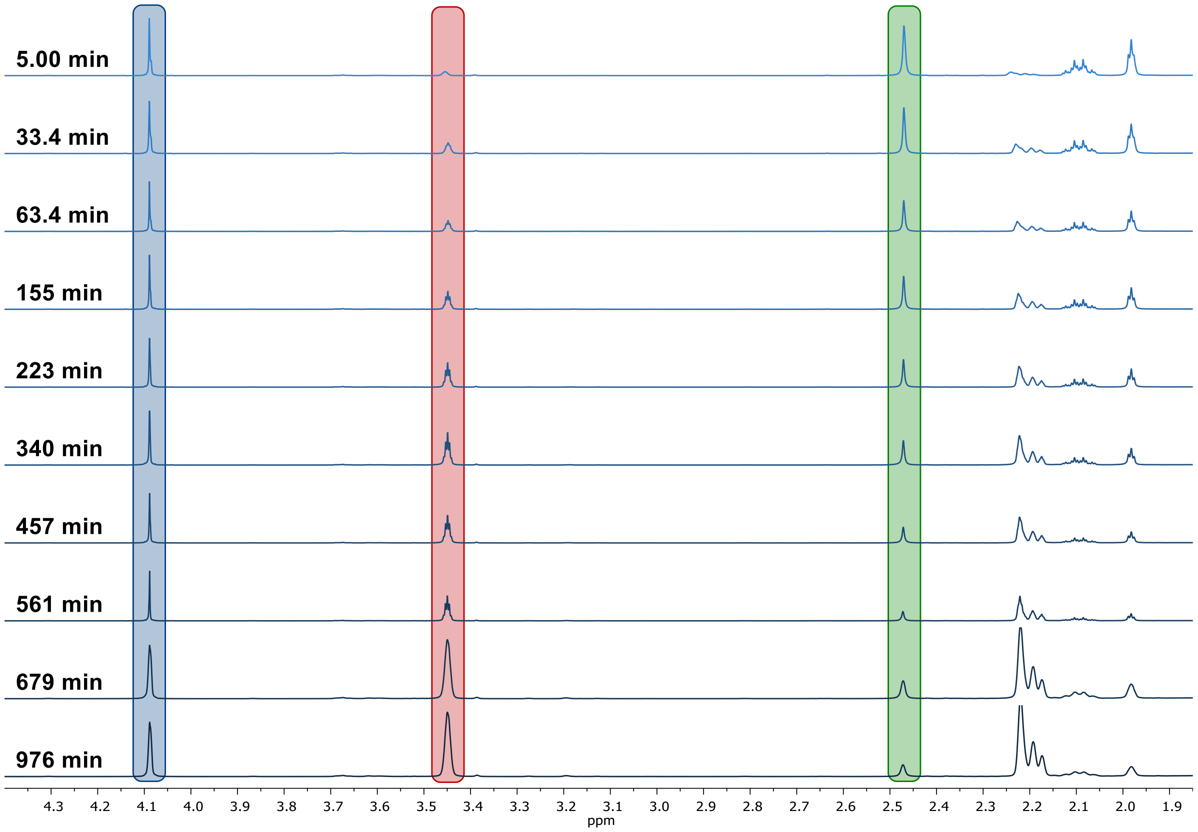


Figure S13: Kinetics were studied for the **Au(I)/Y(III)-SCNP**s catalyzed hydroamination of **1-Me** to **2-Me**. ^{1}H NMR spectra of selected points in time are displayed. The protons used for integration and their corresponding NMR signals were marked in green for the substrate and in red for the product, respectively. The ferrocene (internal standard) NMR signals were marked in blue.

Therefore, for the Au(I)/Y(III)-SCNP catalyzed conversion of **1-Me** to **2-Me** ^{1}H NMR spectra were recorded at 10 min intervals for the first 80 min of the catalysis and then hourly (Figure S13). Substrate **1-Me** was chosen because it features the slowest conversion rates, allowing the most accurate monitoring of the reaction process. The integrals of starting material and product were compared at the respective points in time and normalized to the internal standard (ferrocene). Subsequently, the relative concentrations of starting material and product, respectively, were plotted against the time passed since start of the reaction. Thereby, a first order of the reaction in the starting material was detected.

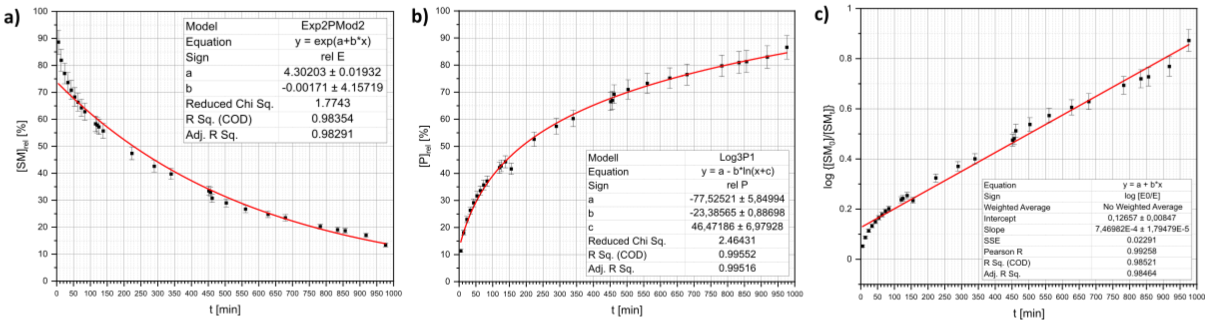


Figure S14 Development of the relative concentration of a) the starting material $[SM]_{rel}$ and b) the product $[P]_{rel}$ [%] with the reaction time t $[min]$ for the reaction of **1-Me** to **2-Me** with 2 mol% of **Au(I)/Y(III)-SCNPs** as catalyst. c) common logarithm of the ratio between the starting material concentration at $t = 0$ ($[SM_0]$) and at t ($[SM_t]$), respectively. For determination of the reaction order, the data points between 13-89% relative starting material concentration (11-87% relative product concentration) were considered.

By evaluation of the recorded ^{1}H NMR spectra and plotting the relative concentration of the starting material $[SM]_{rel}$ against the time, an exponential dependence was observed, whereas the relative concentration of the product $[P]_{rel}$ was increasing logarithmically. This means that the reaction is first order in the starting material. For the experimental determination of the reaction order, the integrated form of the rate law was written in decimal logarithms and plotted. A straight line was obtained in the respective semilogarithmic plot, confirming a first order of the reaction in the starting material.

4 Original Data

4.1 NMR Spectra

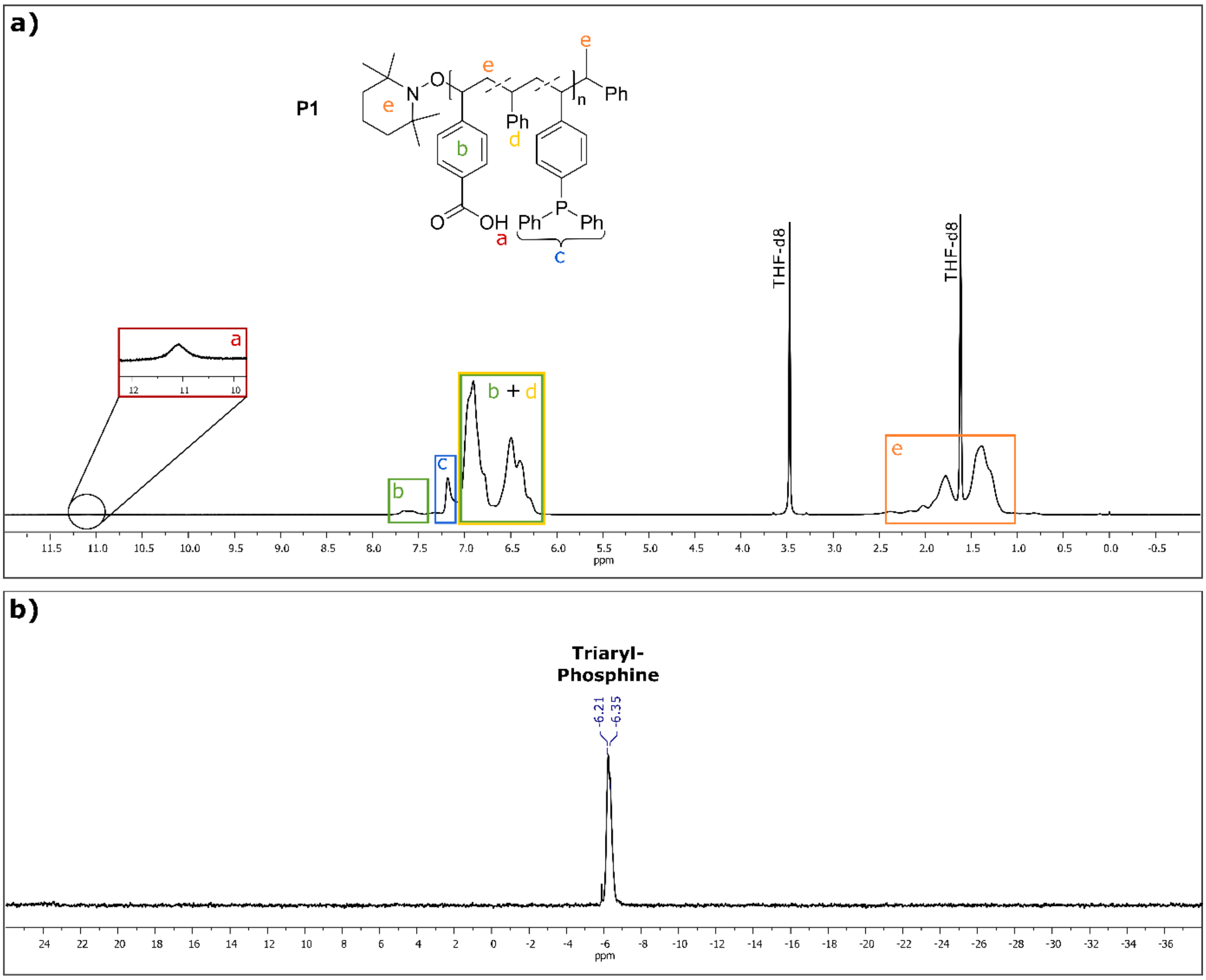


Figure S15: a) ^{1}H NMR spectrum (400 MHz, THF-*d8*) of **P1** with assignment of the resonances. b) ^{31}P{^{1}H} NMR spectrum (162 MHz, THF-d_8) of **P1**. One resonance, attributed to the triaryl-phosphine moieties, was detected at −6.28 ppm.

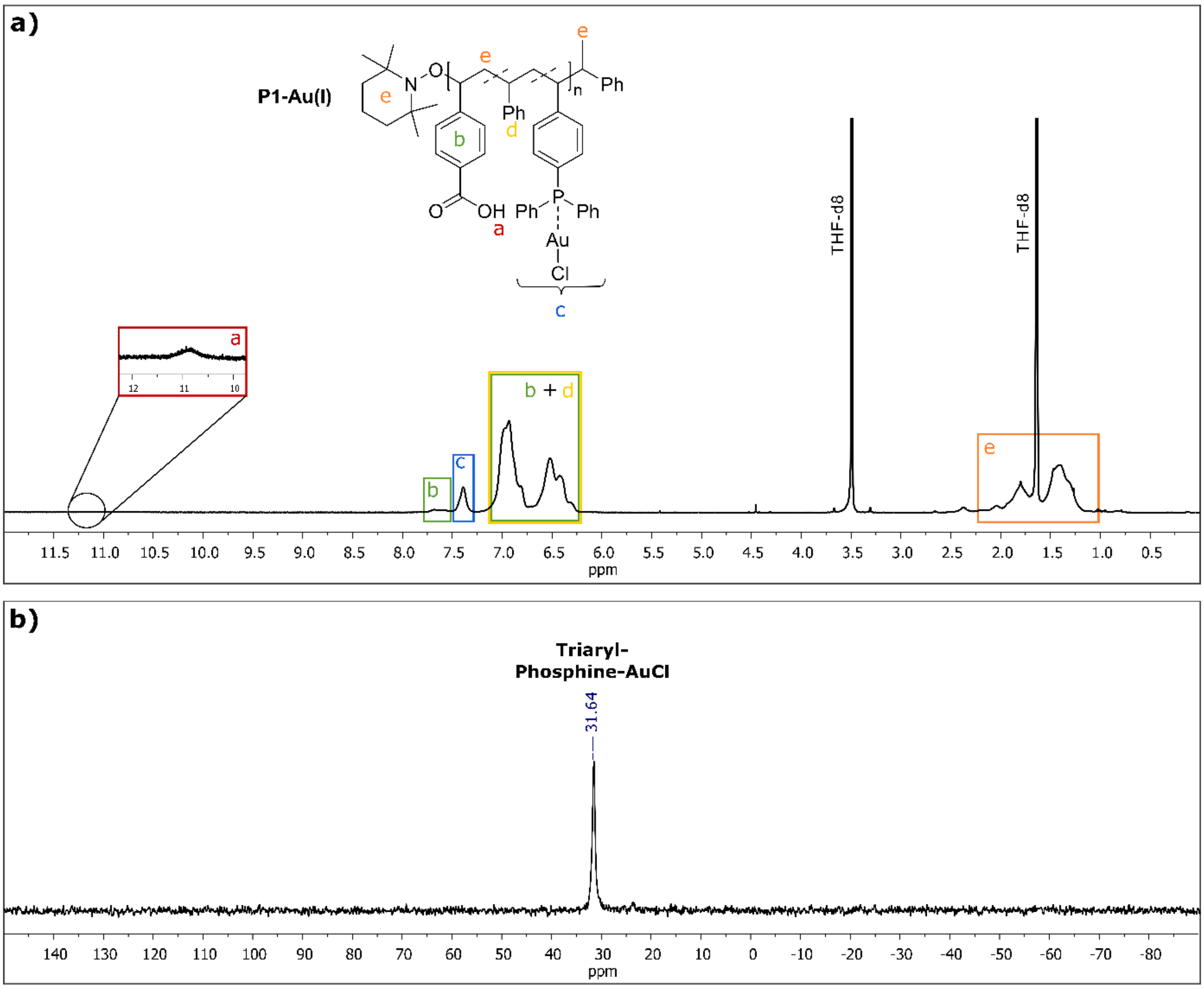


Figure S16: a) ^{1}H NMR spectrum (400 MHz, THF-*d8*) of **P1-Au(I)** with assignment of the resonances. b) ^{31}P{^{1}H} NMR spectrum (162 MHz, THF-*d*$_8$) of **P1-Au(I)**. One resonance, attributed to the triaryl-phosphine-AuCl moieties, was detected at 31.6 ppm.

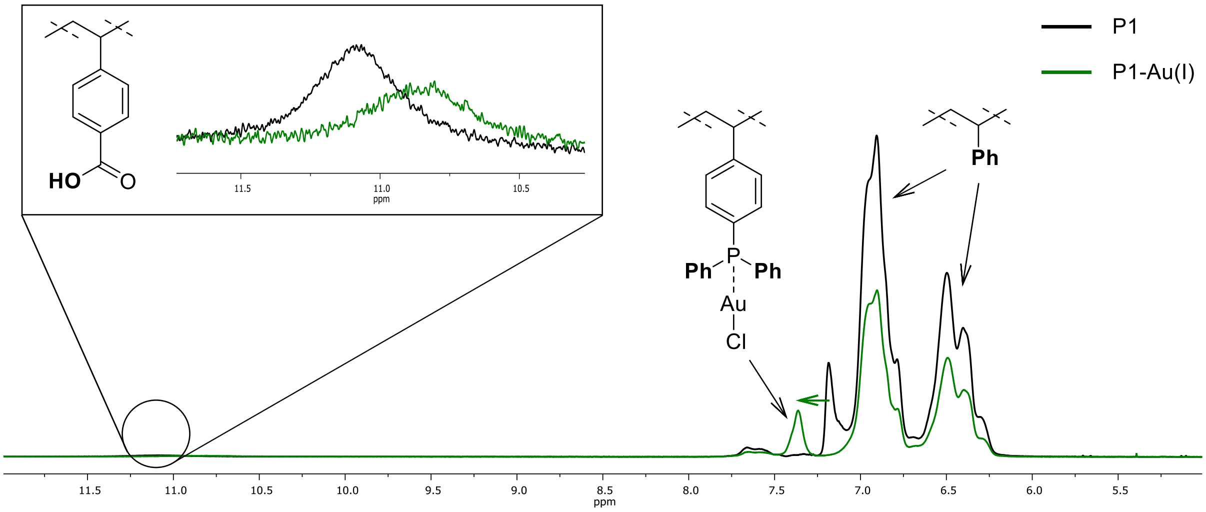


Figure S17: Superimposed ^{1}H NMR spectra of **P1** (black) and **P1-Au(I)** (green) (not normalized). Due to the coordination of AuCl, the resonances of the aromatic protons were shifted towards higher values of δ (lower field).

The broad singulet attributed to the acidic proton of the benzoic acid units is visible for both, **P1** and **P1-Au(I)**, respectively, proving that AuCl selectively coordinates to the phosphine units.

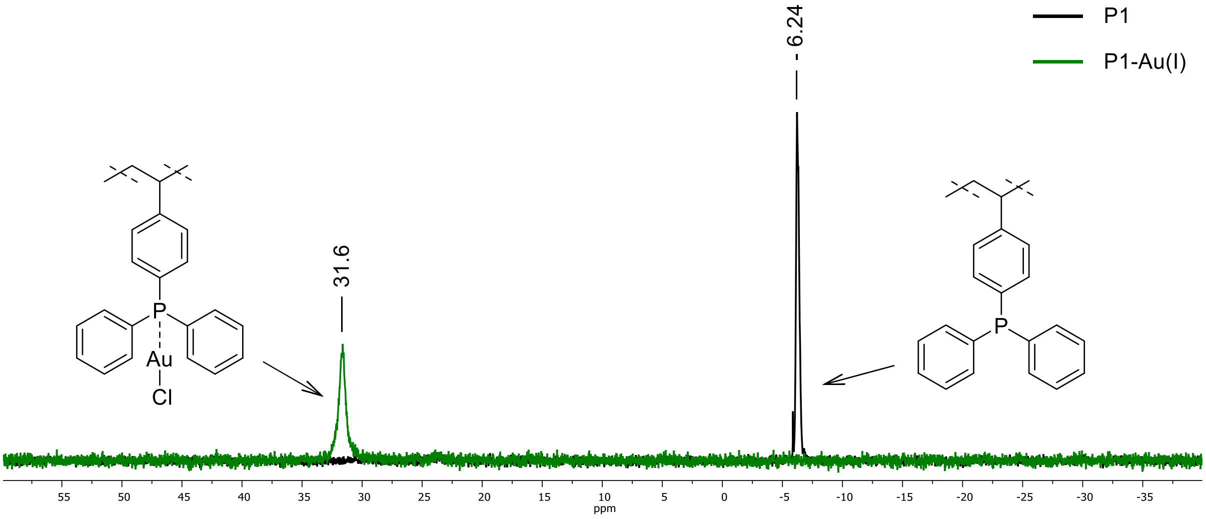


Figure S18: Superimposed $^{31}P\{^1H\}$ NMR spectra of **P1** (black) and **P1-Au(I)** (green) (not normalized). For **P1** a resonance was detected at −6.24 ppm, attributed to the phosphine units. The coordination of AuCl leads to a shift of this resonance towards 31.6 ppm.

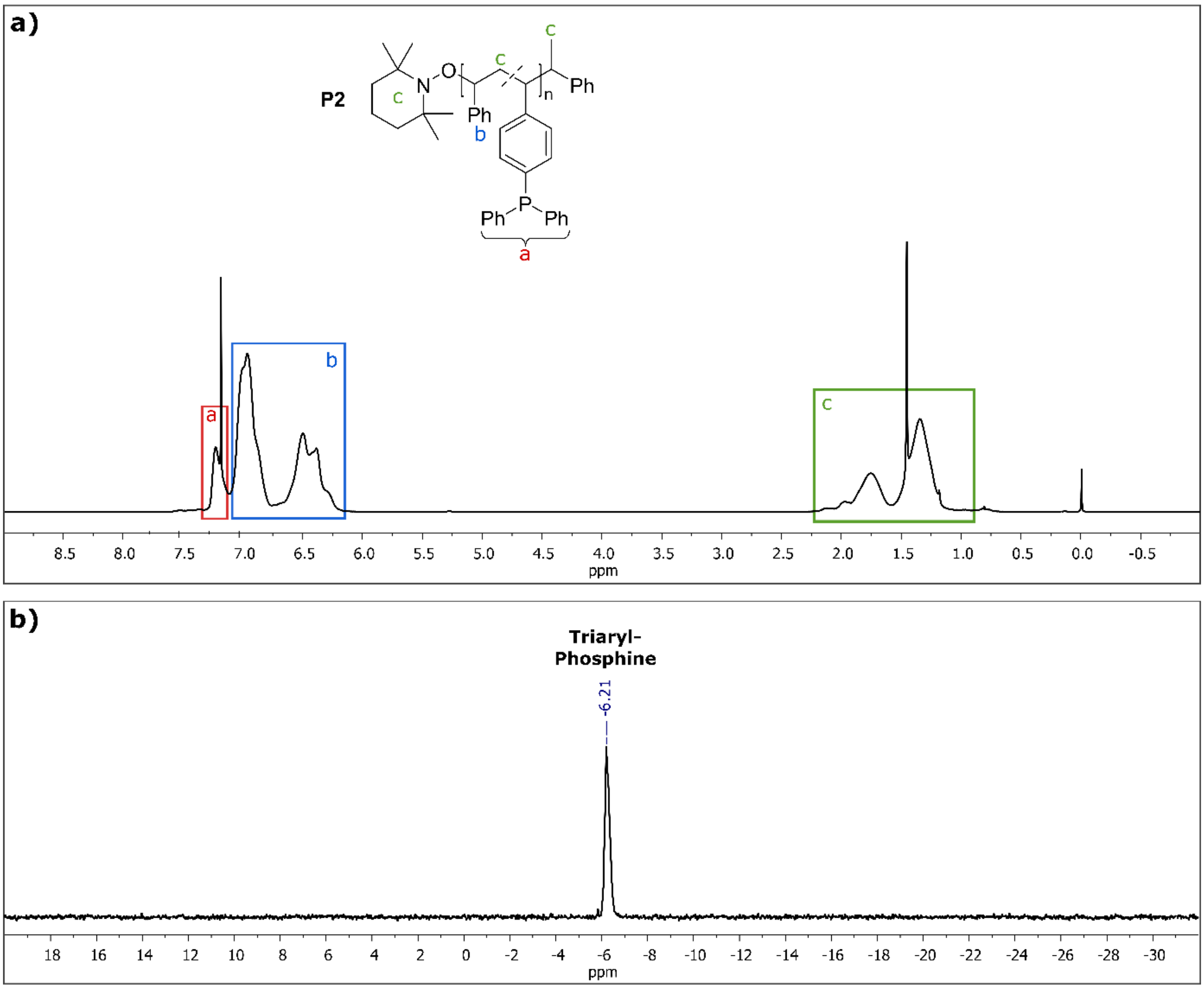


Figure S19: a) ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **P2** with assignment of the resonances. b) ^{31}P{^{1}H} NMR spectrum (162 MHz, CDCl$_3$) of **P2**. One resonance, attributed to the triaryl-phosphine moieties, was detected at −6.21 ppm.

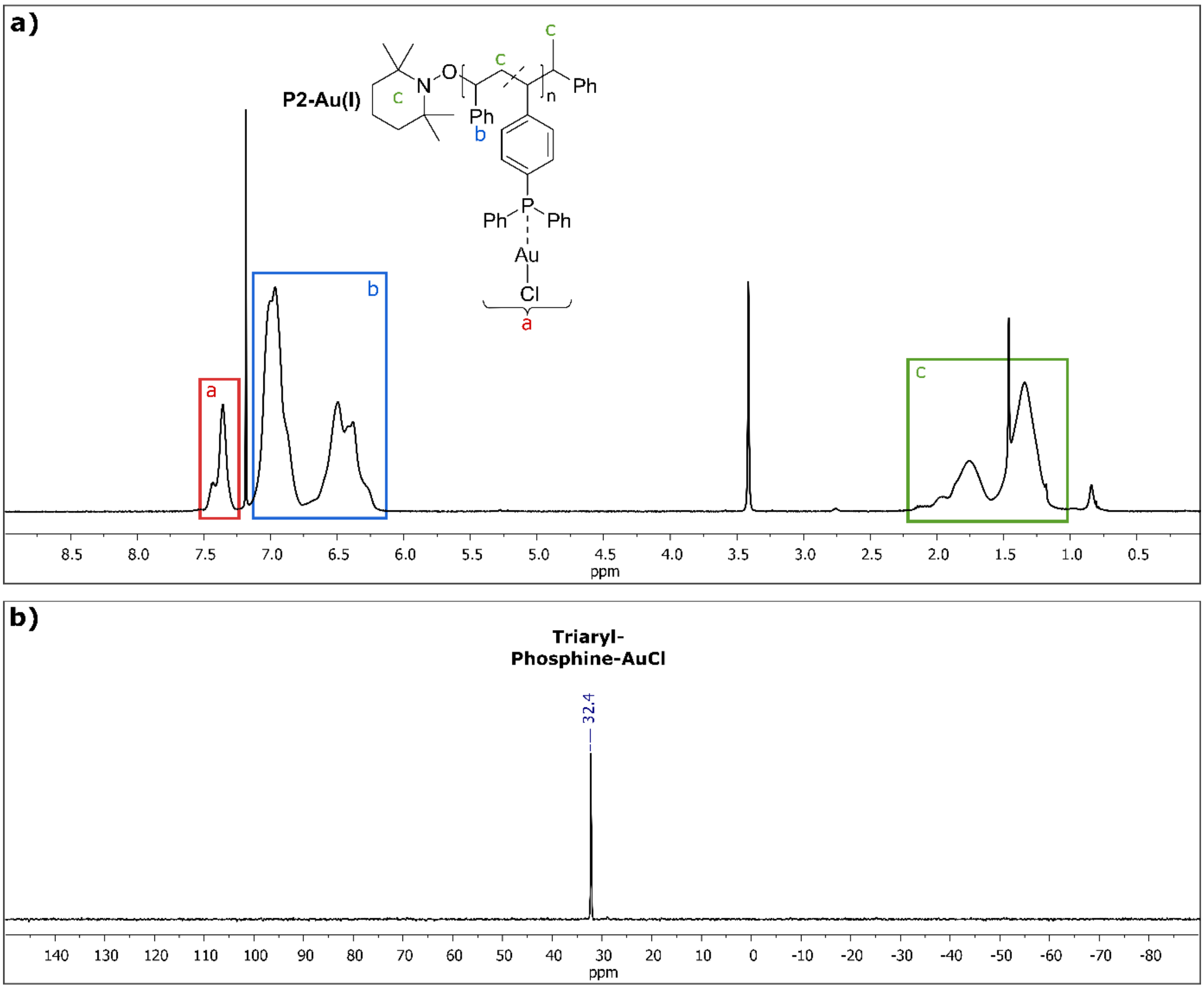


Figure S20: a) ^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **P2-Au(I)** with assignment of the resonances. b) ^{31}P{^{1}H} NMR spectrum (162 MHz, THF-d_8) of **P2-Au(I)**. One resonance, attributed to the triaryl-phosphine-AuCl moieties, was detected at 32.4 ppm.

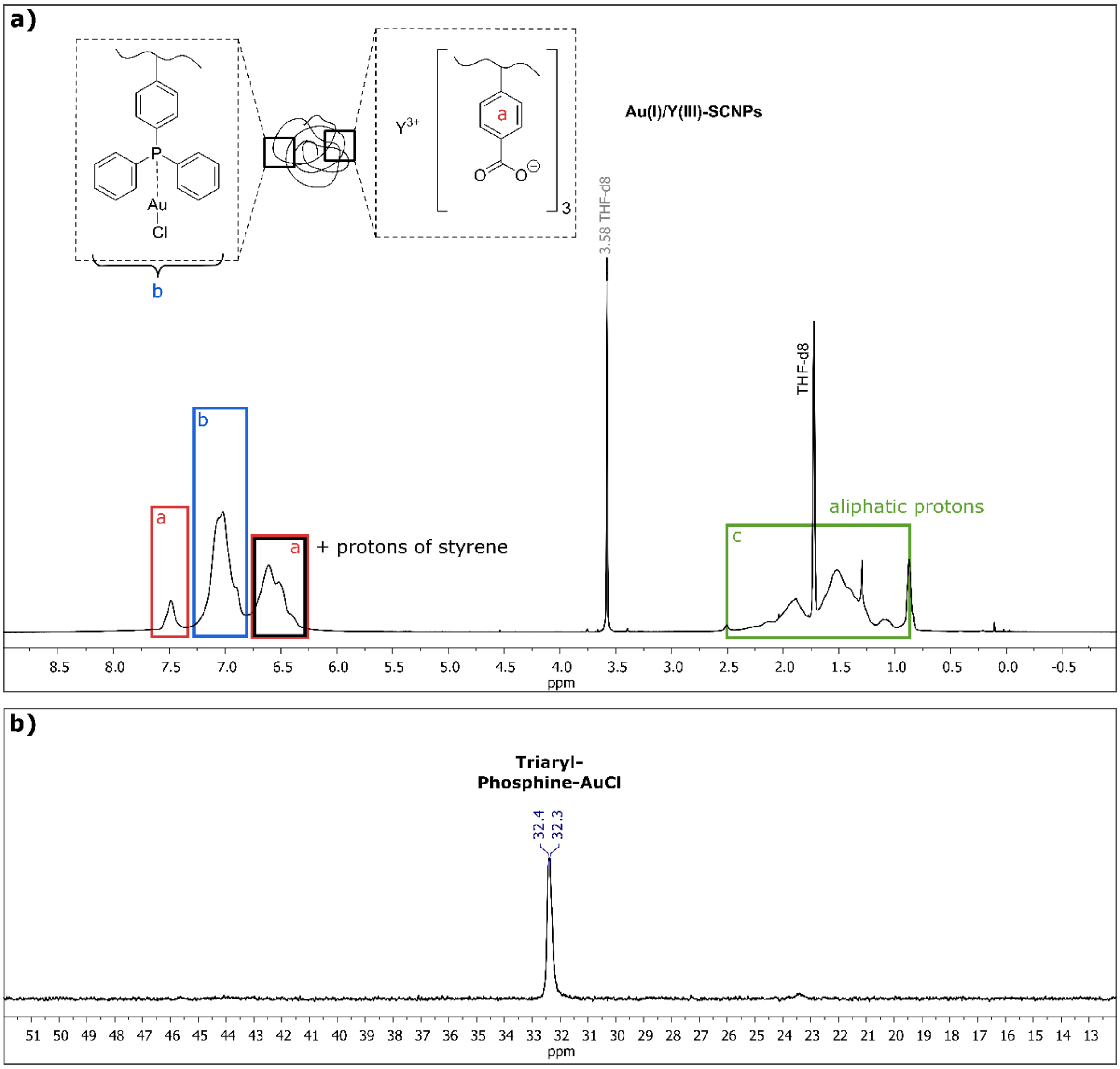


Figure S21: a) ^{1}H NMR spectrum (400 MHz, THF-*d8*) of **Au(I)/Y(III)-SCNPs** with assignment of the resonances. The styrene moieties and aliphatic protons (*e.g.* CH$_2$ groups in the backbone, compare structure of **P1**) are not displayed. b) ^{31}P{^{1}H} NMR spectrum (162 MHz, THF-*d$_8$*) of **P1**. One resonance, attributed to the triaryl-phosphine moieties, was detected at 32.4 ppm.

4.2 SEC Traces

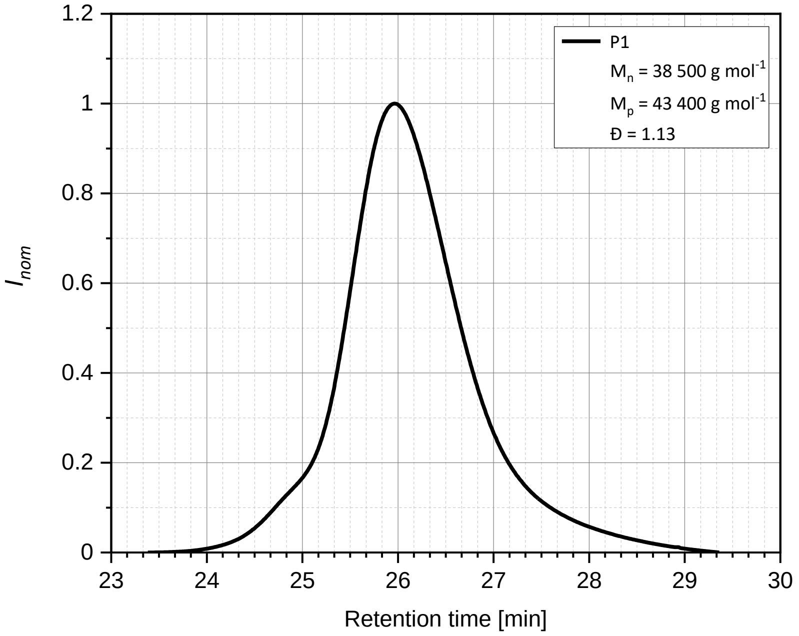


Figure S22: SEC trace of **P1**, with detected molecular weight and dispersity.

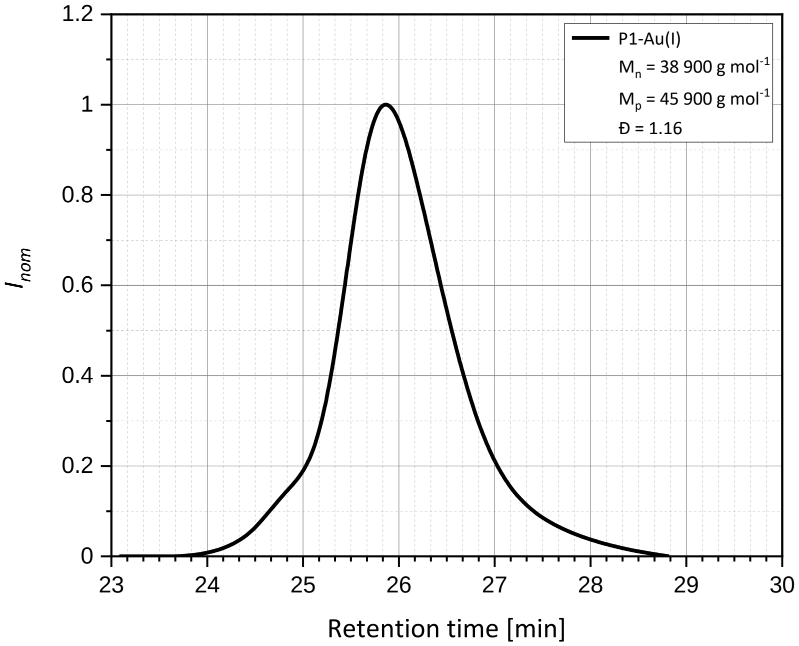


Figure S23: SEC trace of **P1-Au(I)**, with detected molecular weight and dispersity.

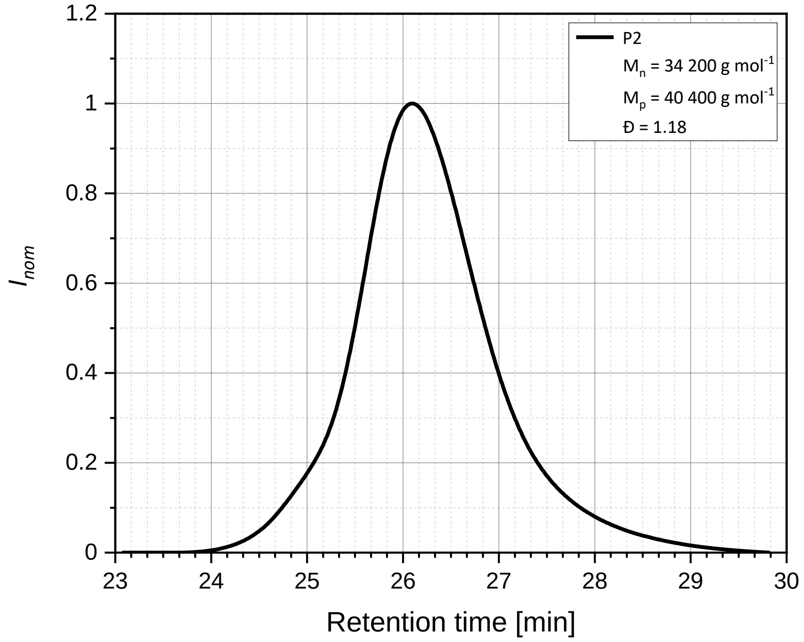


Figure S24: SEC trace of **P2**, with detected molecular weight and dispersity.

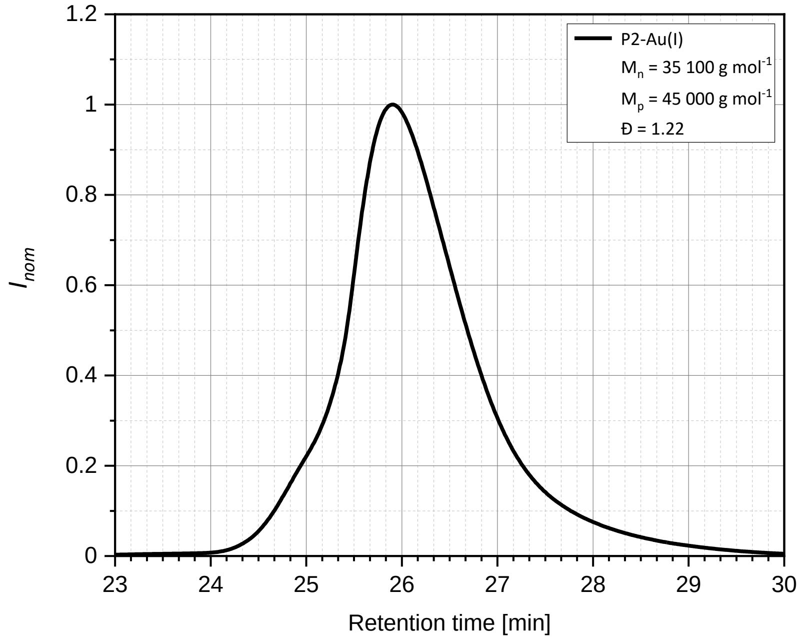


Figure S25: SEC trace of **P2-Au(I)**, with detected molecular weight and dispersity.

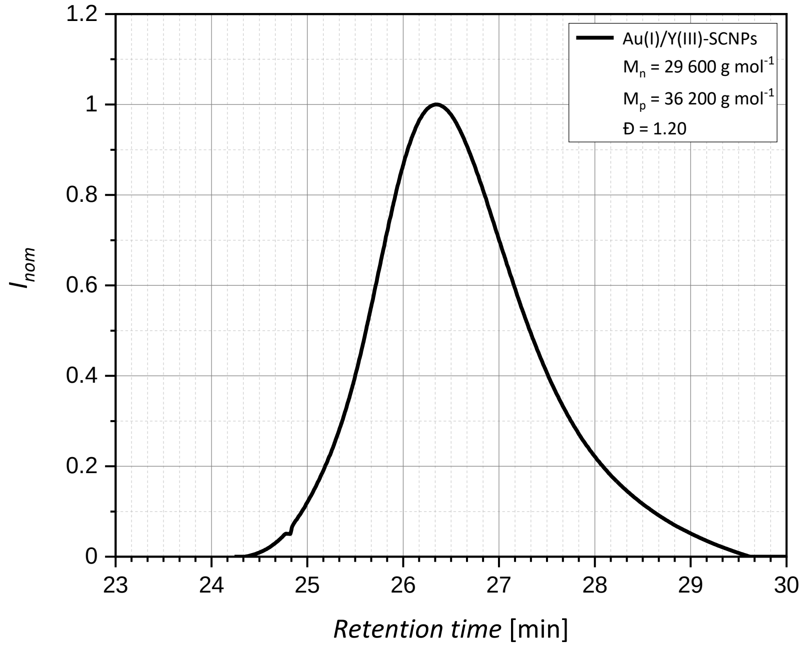


Figure S26: SEC trace of **Au(I)/Y(III)-SCNPs**, with detected molecular weight and dispersity.

4.3 IR Spectra

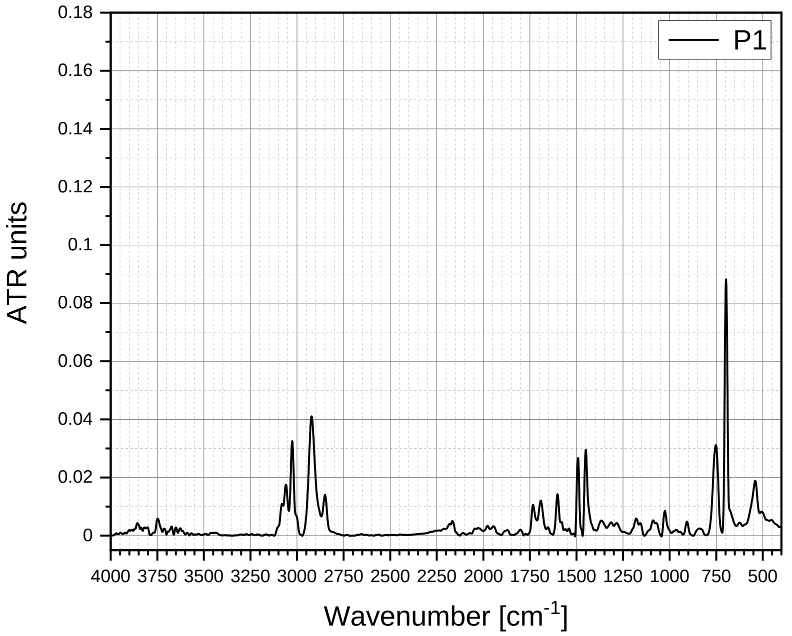


Figure S27: IR spectrum of **P1**.

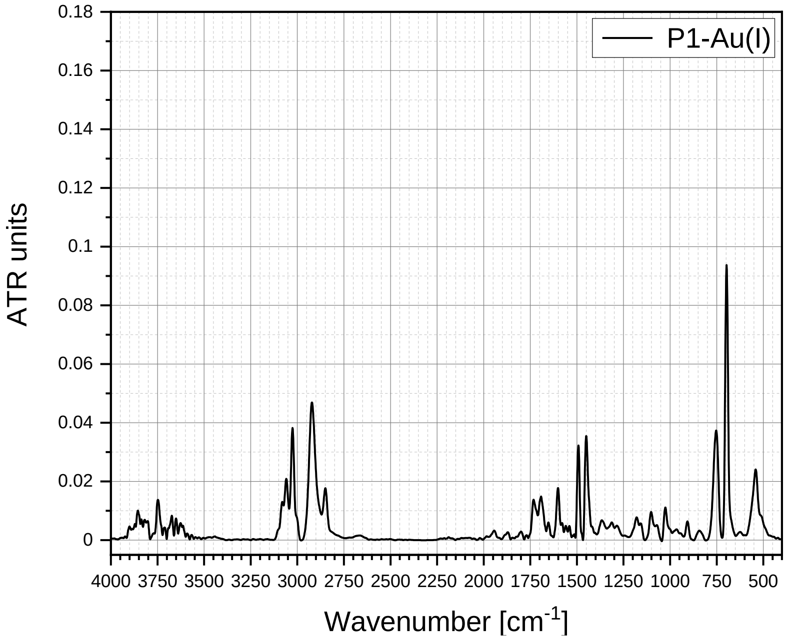


Figure S28: IR spectrum of **P1-Au(I)**.

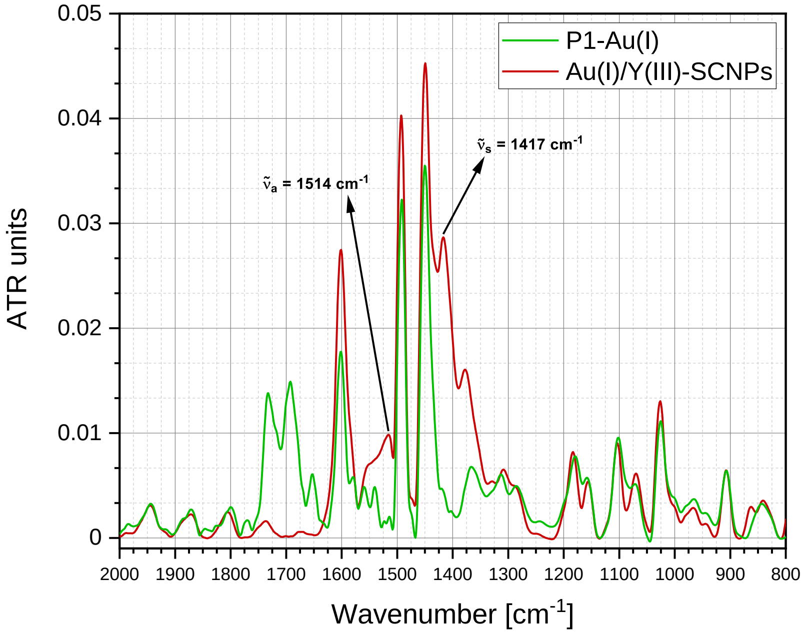


Figure S29: Superimposed IR spectra of **P1-Au(I)** and **Au(I)/Y(III)-SCNPs**. Bands of the C=O vibrational at $\tilde{\nu}$ = 1660-1750 cm^{-1}, attributed to the free carboxylic acid units, were not detected anymore for the SCNPs. Instead, two new bands at $\tilde{\nu}_a$ = 1514 und $\tilde{\nu}_s$ = 1417 cm^{-1} were observed demonstrating the carboxylate complexation of the Y(III) ions. The unchanged $\nu_{\text{P-C(q-vib)}}$-band at $\tilde{\nu}$ = 1103 cm^{-1} further proves the [ArPPh$_2$P-AuCl] moieties to be intact. Only the relevant range of the spectrum is displayed.

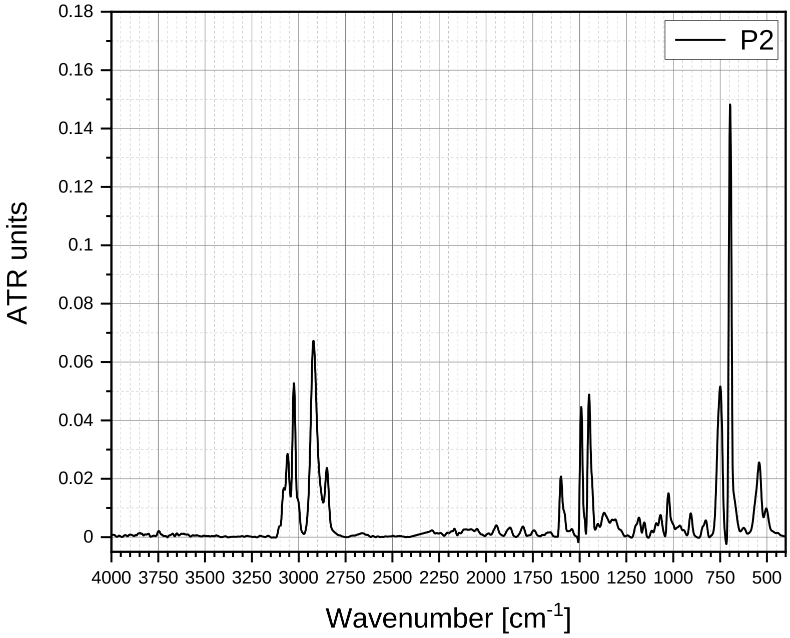


Figure S30: IR spectrum of **P2**.

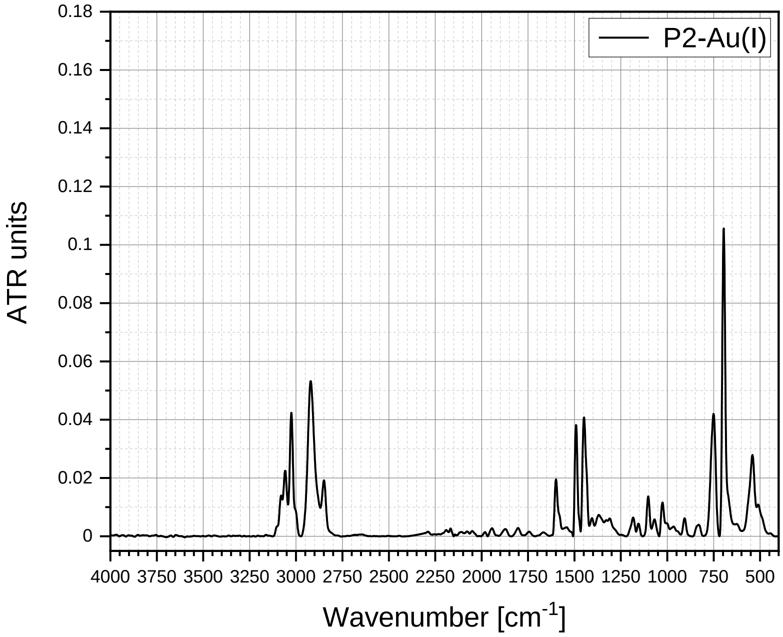


Figure S31: IR spectrum of **P2-Au(I)**.

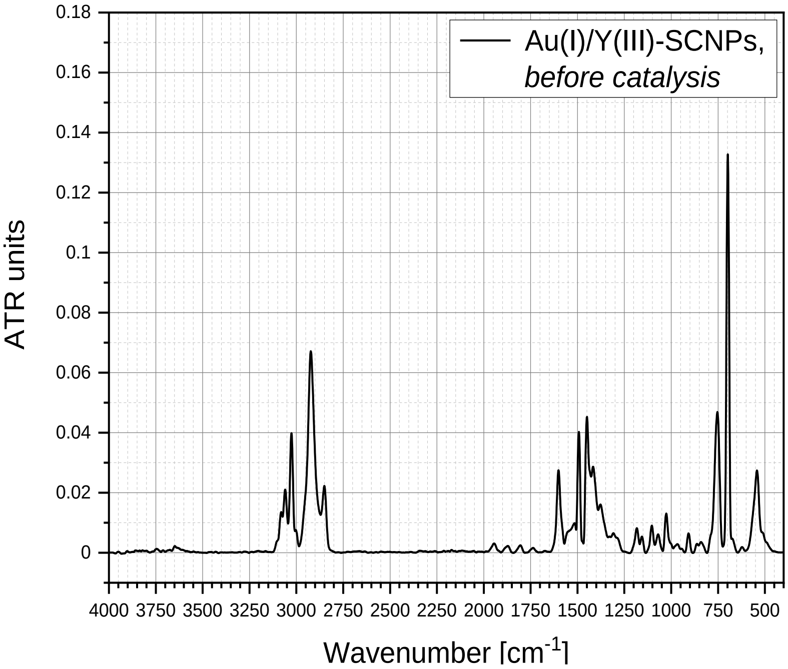


Figure S32: IR spectrum of **Au(I)/Y(III)-SCNPs** before catalysis.

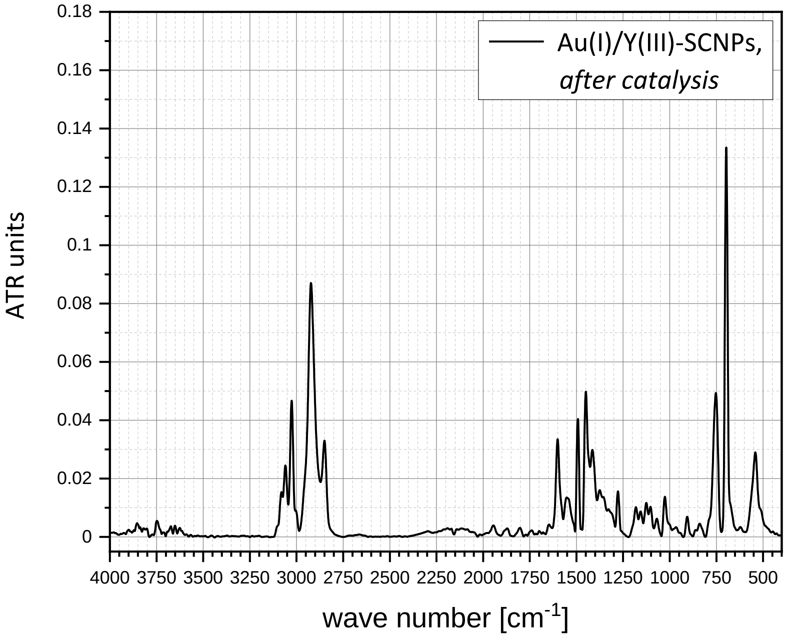


Figure S33: IR spectrum of **Au(I)/Y(III)-SCNPs** after catalysis. Compared to the IR spectrum of the SCNPs before catalysis (Figure S 32).