Unsaturated Vicinal Frustrated Phosphane/Borane Lewis Pairs as Ligands in Gold(I) Chemistry

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Supporting Information

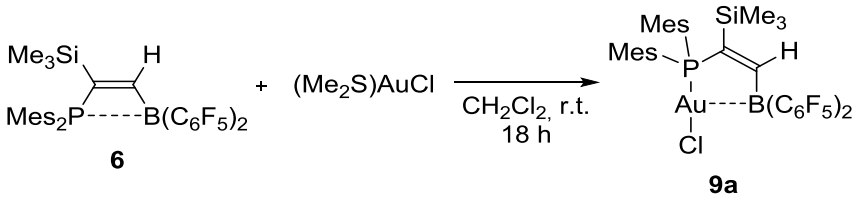
General Information: all syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glovebox) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on a Varian Inova 500 (^{1}H 500 MHz, ^{13}C 126 MHz, ^{19}F 470 MHz, ^{11}B 160 MHz, ^{31}P 202 MHz, ^{29}Si 99 MHz) and on a Varian UnityPlus 600 (^{1}H 600 MHz, ^{13}C 151 MHz, ^{19}F 564 MHz, ^{11}B 192 MHz, ^{31}P 243 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, δ = 0), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, δ = 0), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in D_2O) (external reference, δ = 0). NMR assignments were supported by additional 2D-NMR experiments. The isotope-induced chemical shift (IECS) was calculated by using $\Delta\delta^{31}P(^{10/11}B) = \delta^{31}P(^{11}B) - \delta^{31}P(^{10}B)$ and given in ppb [B. Wrackmeyer, G. Seidel, R. Köster, *Magn. Reson. Chem.* 2000, **38**, 520-524. See also: P. E. Hansen, *Prog. NMR Spectrosc.* 1988, **20**, 207-255]. Elemental analyses: Foss–Heraeus CHNO-Rapid.

X-Ray diffraction: For compounds **9b** (erk9092) and **10a** (erk9204) data sets were collected with a Nonius Kappa CCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* 1997, **276**, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. 2003, **A59**, 228-234); Data sets for compounds **9a** (erk8894) and **10b** (erk9161) were collected with a D8 Venture CMOS diffractometer. Programs used: data collection: APEX3 V2016.1-0 (Bruker AXS Inc., 2016); cell refinement: SAINT V8.37A (Bruker AXS Inc., 2015); data reduction: SAINT V8.37A (Bruker AXS Inc., 2015); absorption correction, SADABS V2014/7 (Bruker AXS Inc., 2014); structure solution SHELXT-2015 (Sheldrick, 2015); structure refinement SHELXL-2015 (Sheldrick, **2015**) and graphics, XP (Bruker AXS Inc., 2015). *R*-values are given for observed reflections, and wR^2 values are given for all reflections. *Exceptions and special features*: For compound **10b** (erk9161) the $-NTf_2$ group and for compound **10a** (erk9204) two CF_3 groups were found disordered over two positions in the asymmetric unit. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability. For compounds **10a** (erk9204) and **10b** (erk9161) a badly disordered half pentane molecule and for compound **9b** (erk9092) probably a mixture of a half pentane molecule and a small amount of dichloromethane molecule were found in the asymmetrical unit and could not be satisfactorily refined. The program SQUEEZE (Spek, A.L. Acta Cryst. 2015, **C71**, 9-18) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters do not include the squeezed solvent molecule.

Materials: Compound **6** and **8** were synthesized according to procedures described in the following literature [A. Ueno, X. Tao, C. G. Daniliuc, G. Kehr, G. Erker, Unusual 1,1-Hydroboration Route to a Reactive Unsaturated Vicinal Frustrated Phosphine/Borane Lewis Pair, *Organometallics*, 2018, **37**, 2665].

Note: p-toluidine is toxic by inhalation, in contact with skin and if swallowed.

Preparation of compound 9a:



Scheme S1

A solution of compound **6** (180 mg, 0.25 mmol) and (Me_2S)AuCl (80 mg, 0.26 mmol) in CH_2Cl_2 (3 mL) was stirred for 18 hours at room temperature. Then, all volatiles were removed *in vacuo* and *n*-pentane (2 mL) was added. The bright yellow precipitate of the resulting suspension was collected, washed with *n*-pentane (2 mL × 2) and dried *in vacuo* to give compound **9a** as a bright yellow powder (186 mg, 0.20 mmol, 79%).

Elemental Analysis calcd for $C_{35}H_{32}AuBClF_{10}PSi$ (944.91 g/mol): C, 44.49; H, 3.41. Found: C, 44.70; H, 3.21.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.29 (md, $^{3}J_{PH}$ = 96.2 Hz, 1H, BCH=), 6.88 (m, 4H, *m*-Mes), 2.45 (br, 12H, *o*-Me^{Mes}), 2.31 (s, 6H, *p*-Me^{Mes}), 0.04 (s, $^{2}J_{SiH}$ = 6.6 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 178.3 (br, BCH=),147.5 (dm, $^{1}J_{FC}$ ~ 242 Hz, C_6F_5), 143.17 (d, $^{4}J_{PC}$ = 2.2 Hz, *p*-Mes), 143.15 (dm, $^{1}J_{FC}$ ~ 257 Hz, C_6F_5), 142.7 (d, $^{2}J_{PC}$ = 24.3 Hz, PC=), 141.9 (d, $^{2}J_{PC}$ = 9.9 Hz, *o*-Mes), 137.5 (dm, $^{1}J_{FC}$ ~ 252 Hz, C_6F_5), 131.8 (d, $^{3}J_{PC}$ = 9.9 Hz, *m*-Mes), 123.8 (d, $^{4}J_{PC}$ = 55.7 Hz, *i*-Mes), 116.0 (br, C_6F_5), 24.9 (d, $^{3}J_{PC}$ = 9.4 Hz, *o*-Me^{Mes}), 20.9 (*p*-Me^{Mes}), 0.35 ($SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = 34.2 ($\nu_{1/2}$ ~ 1000 Hz).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 34.2 ($\nu_{1/2}$ ~ 1000 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = 43.9 (d, $^{3}J_{PH}$ ~ 98 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 43.9165 (^{31}P(^{10}B), 18 mol%), 43.9007 (^{31}P(^{11}B), 82 mol%), [$\Delta^{10/11}$B(^{31}P) = -15.8 ppb].

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -125.8 (m, 4F, *o*-C_6F_5), -152.1 (m, 2F, *p*-C_6F_5), -163.4 (m, 4F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{m,\,p}$ = 11.2].

^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 299 K): δ = -0.7 (d, $^{2}J_{PSi}$ = 14.3 Hz).

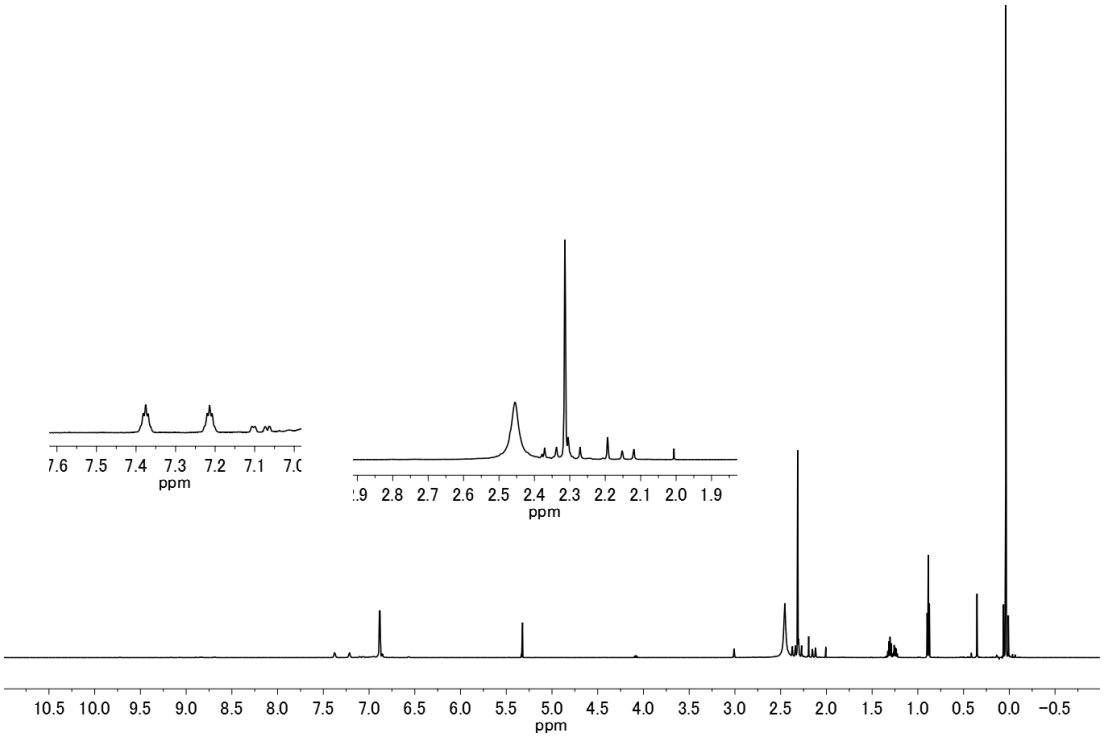


Figure S1 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **9a**

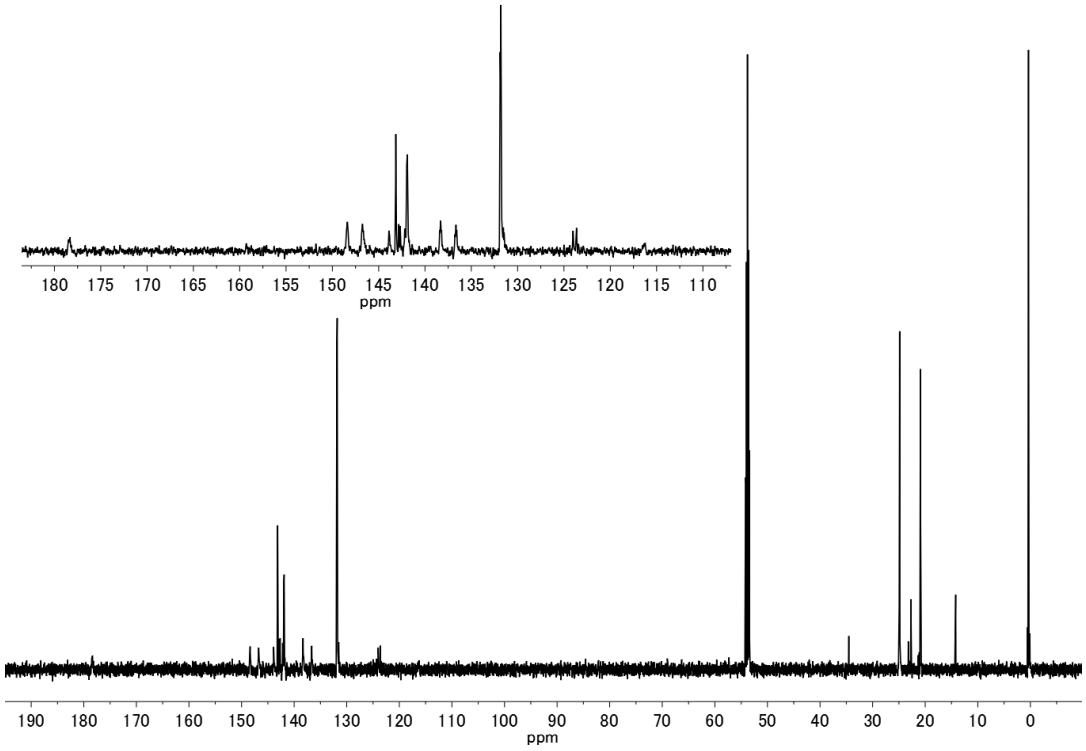


Figure S2 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **9a**

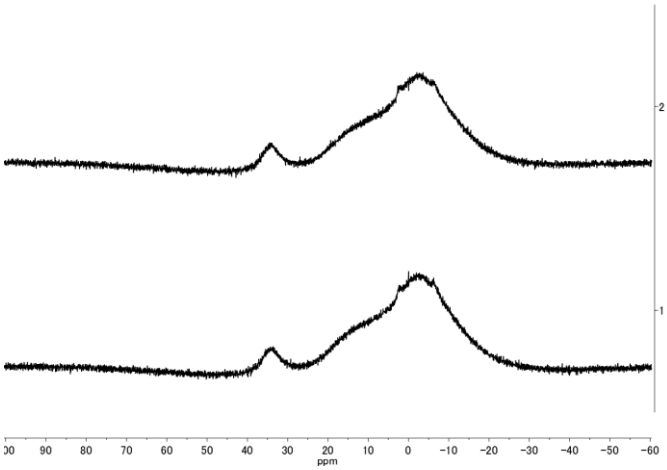


Figure S3 (1) **^{11}B{^{1}H}** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **9a**

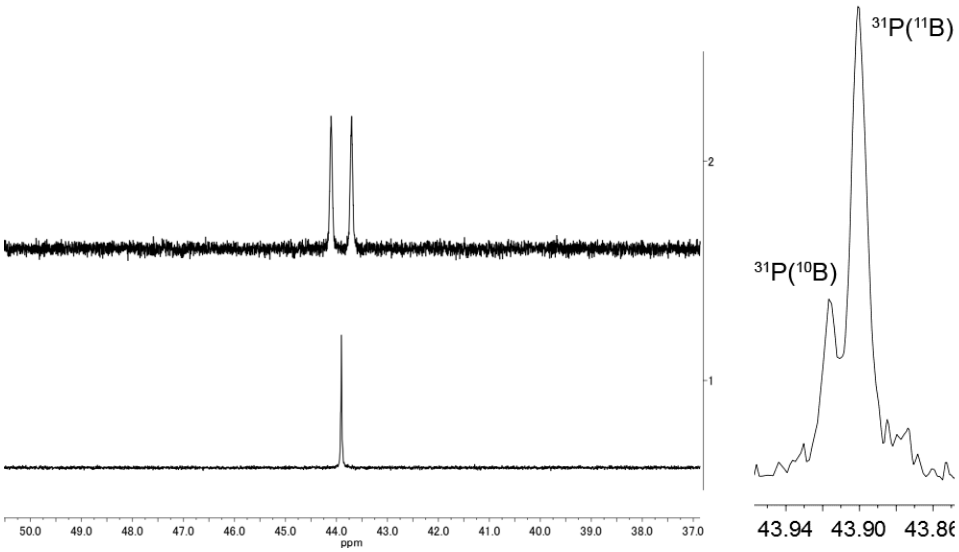


Figure S4 (1) **^{31}P{^{1}H}** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299 K) spectra of compound **9a**

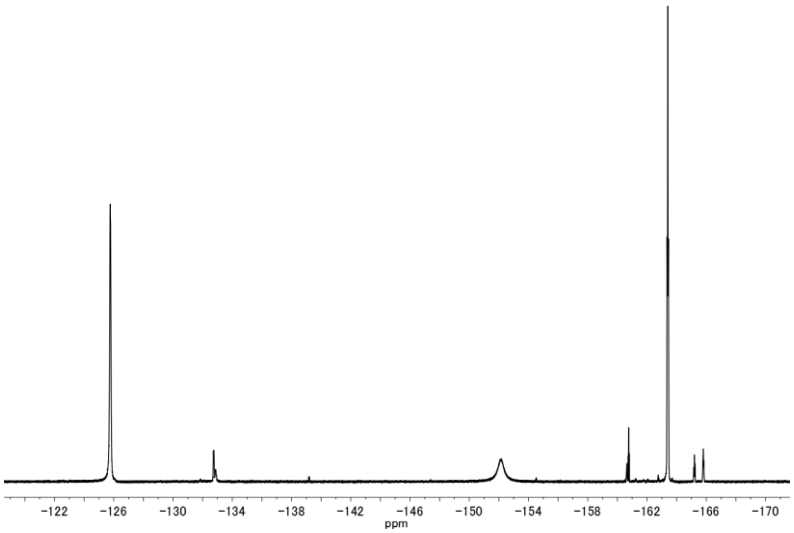


Figure S5 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **9a**

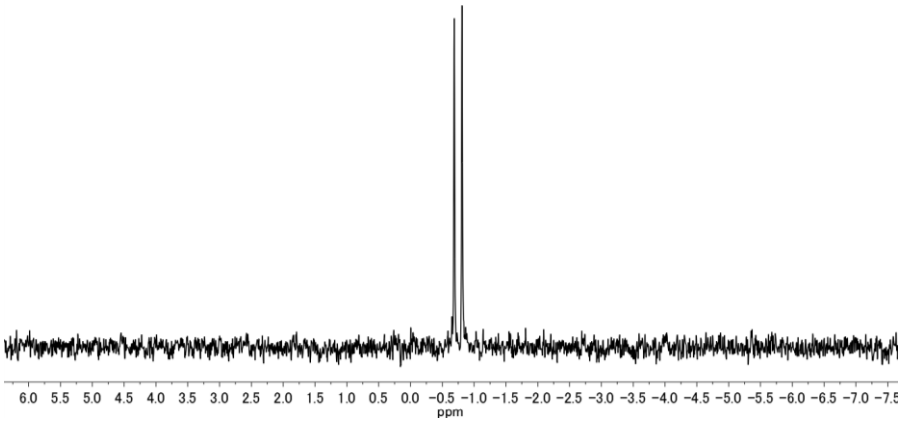


Figure S6 **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **9a**

Crystals suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane into a saturated solution of compound **9a** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 9a (8894.ERK): A colorless prism-like specimen of $C_{35}H_{32}AuBClF_{10}PSi$, approximate dimensions 0.113 mm x 0.118 mm x 0.121 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 505 frames were collected. The total exposure time was 3.71 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 44054 reflections to a maximum θ angle of 25.03° (0.84 Å resolution), of which 6160 were independent (average redundancy 7.152, completeness = 99.7%, R_{int} = 16.59%, R_{sig} = 8.62%) and 4508 (73.18%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.168(3) Å, b = 13.267(3) Å, c = 20.346(4) Å, β = 100.339(6)°, volume = 3496.7(12) Å^3, are based upon the refinement of the XYZ-centroids of 9924 reflections above 20 σ(I) with 5.075° < 2θ < 51.36°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.740. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6150 and 0.6340. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 4 for the formula unit, $C_{35}H_{32}AuBClF_{10}PSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 460 variables converged at R1 = 7.68%, for the observed data and wR2 = 16.94% for all data. The goodness-of-fit was 1.198. The largest peak in the final difference electron density synthesis was 1.904 e^-/Å^3 and the largest hole was -3.035 e^-/Å^3 with an RMS deviation of 0.247 e^-/Å^3. On the basis of the final model, the calculated density was 1.795 g/cm^3 and F(000), 1848 e^-.

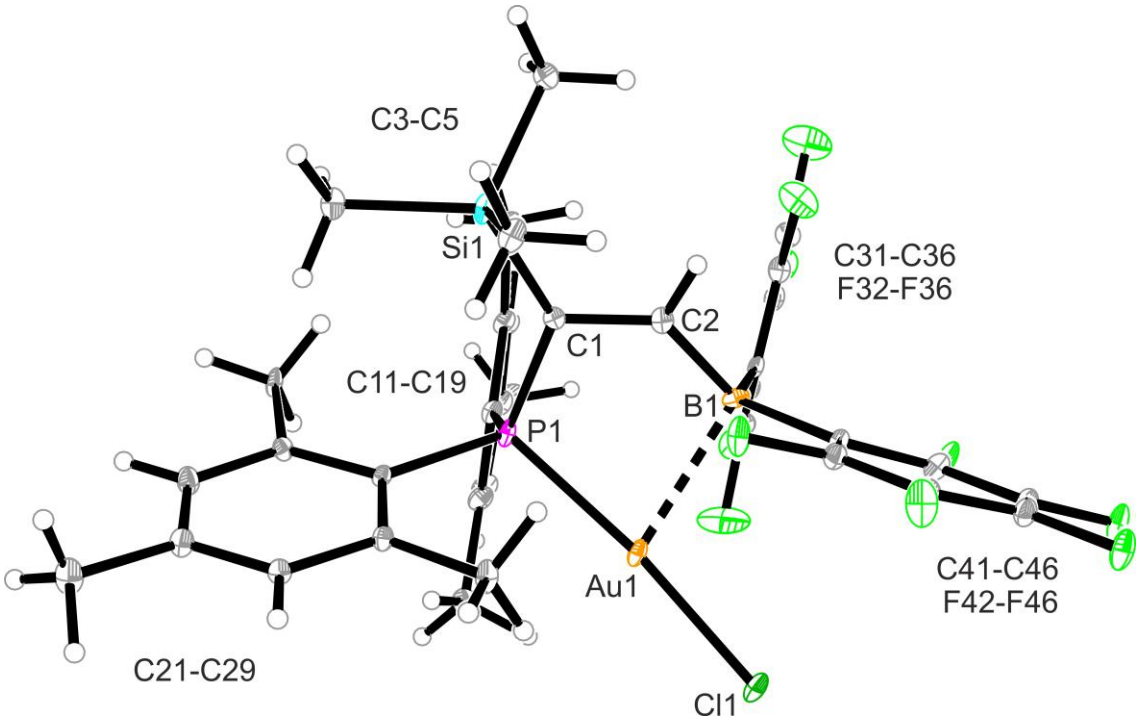
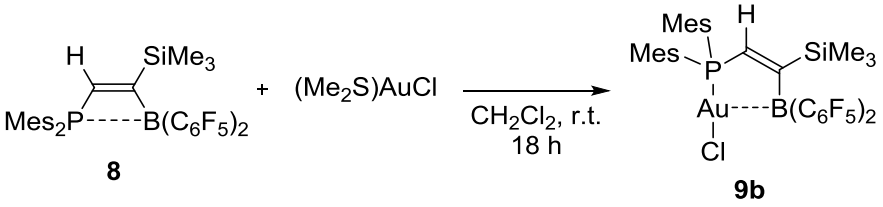


Figure S7

(Thermal ellipsoids are shown with 15% probability)

Preparation of compound 9b:



Scheme S2

A mixture of compound **8** (100 mg, 0.14 mmol) and $(Me_2S)AuCl$ (42 mg, 0.14 mmol) in CH_2Cl_2 (1 mL) was stirred for 18 hours at room temperature. Then, all volatiles were removed *in vacuo* and *n*-pentane (2 mL) was added and stirred for 10 minutes. The white precipitate of the resulting suspension was collected, washed with *n*-pentane (2 mL × 2) and dried *in vacuo* to give compound **9b** as a white powder (102 mg, 0.11 mmol, 77%).

Elemental Analysis calcd for $C_{35}H_{32}AuBClF_{10}PSi$ (944.91 g/mol): C, 44.49; H, 3.41. Found: C, 44.30; H, 3.25.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.06 (d, $^{2}J_{PH}$ = 24.0 Hz, 1H, PCH=), 6.88 (m, 4H, *m*-Mes), 2.38 (s, 12H, *o*-Me^{Mes}), 2.30 (s, 6H, *p*-Me^{Mes}), 0.07 (s, $^{2}J_{SiH}$ = 7.2 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 174.6 (br, BC=), 148.5 (dm, $^{1}J_{FC}$ ~ 253 Hz, C_6F_5), 144.6 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 142.34 (d, $^{2}J_{PC}$ = 9.9 Hz, *o*-Mes), 142.27 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes), 139.5 (d, $^{1}J_{PC}$ = 48.8 Hz, PCH=), 137.7 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 131.8 (d, $^{3}J_{PC}$ = 9.3 Hz, *m*-Mes), 124.9 (d, $^{1}J_{PC}$ = 55.3 Hz, *i*-Mes), 114.0 (br m, C_6F_5), 24.5 (d, $^{3}J_{PC}$ = 8.9 Hz, *o*-Me^{Mes}), 20.9 (m, *p*-Me^{Mes}), -0.69 ($SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = 54.8 (br, $\nu_{1/2}$ ~ 1000 Hz).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 54.8 (br, $\nu_{1/2}$ ~ 1000 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = 19.8 (d, $^{2}J_{PH}$ ~ 24 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 19.7980 (^{31}P(^{10}B), 19 mol%), 19.7505 (^{31}P(^{11}B), 81 mol%), [$\Delta^{10/11}$B(^{31}P) = -47.5 ppb].

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -123.0 (m, 4F, *o*-C_6F_5), -146.8 (mt, $^{3}J_{FF}$ = 21.7 Hz, 2F, *p*-C_6F_5), -162.1 (m, 4F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{m,\,p}$ = 15.3].

^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 299 K): δ = -0.6 (d, $^{3}J_{PSi}$ = 32.3 Hz).

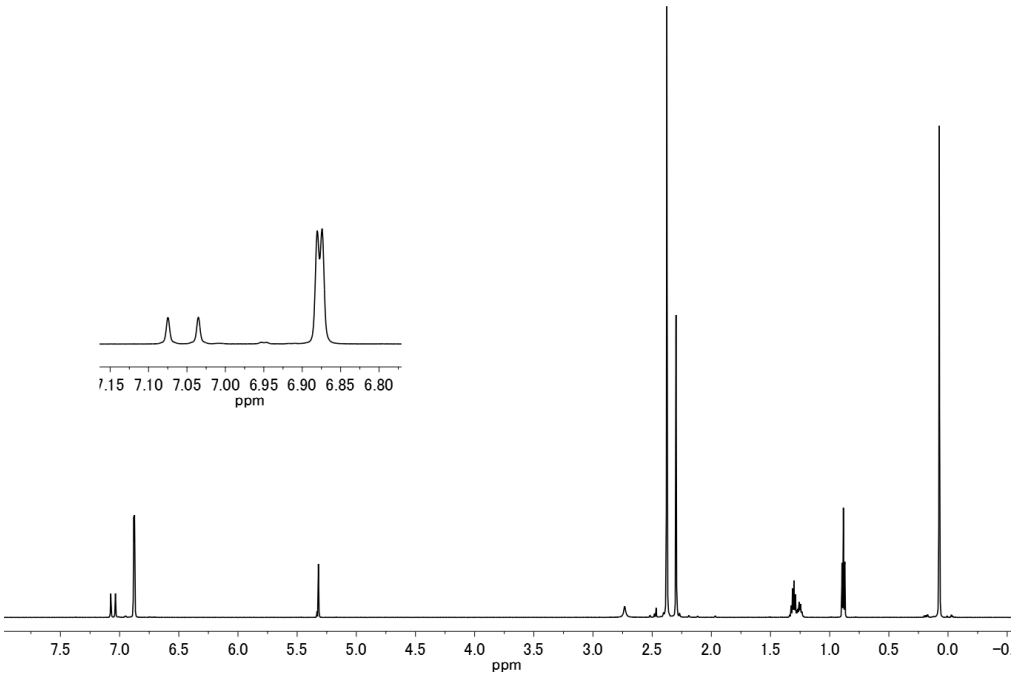


Figure S8 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **9b**

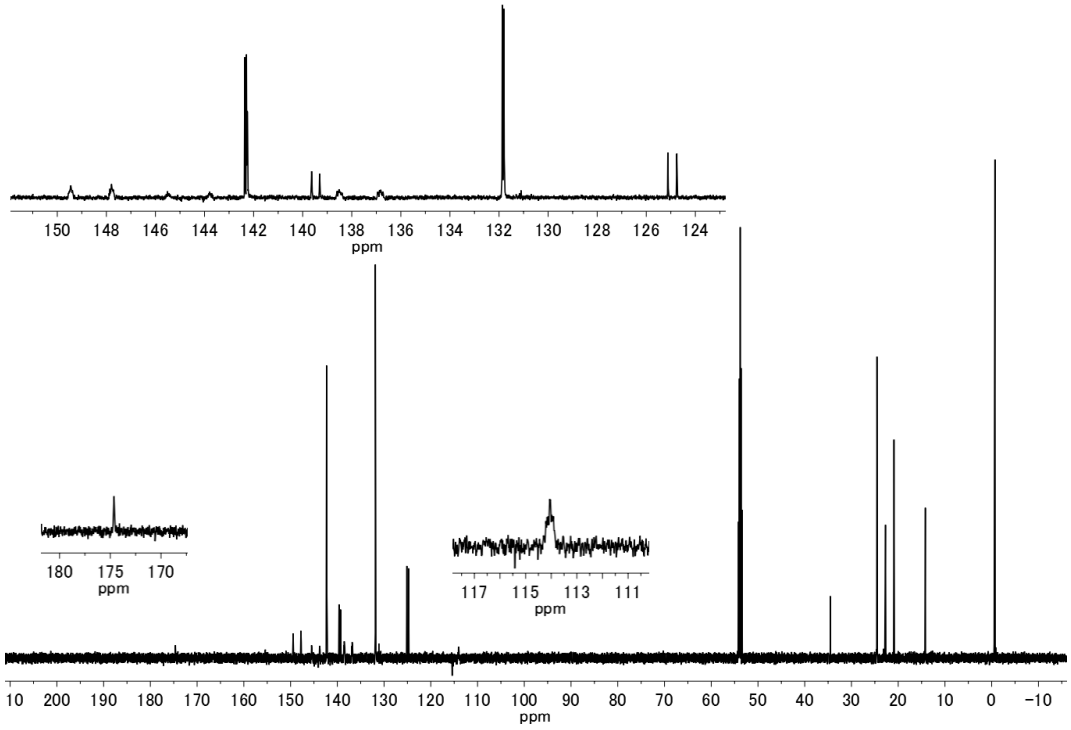


Figure S9 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **9b**

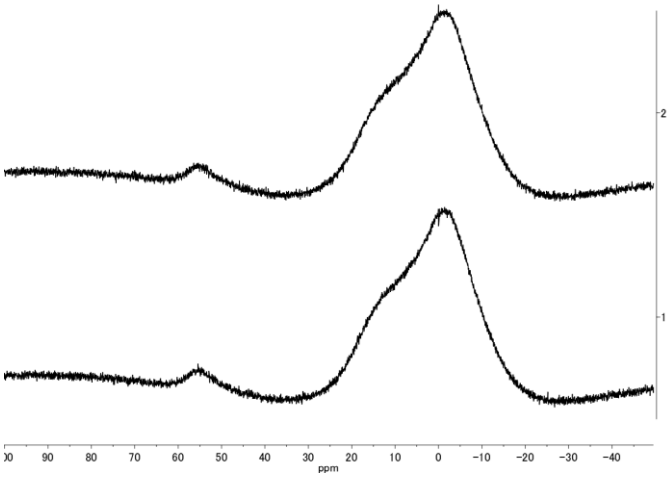


Figure S10 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **9b**

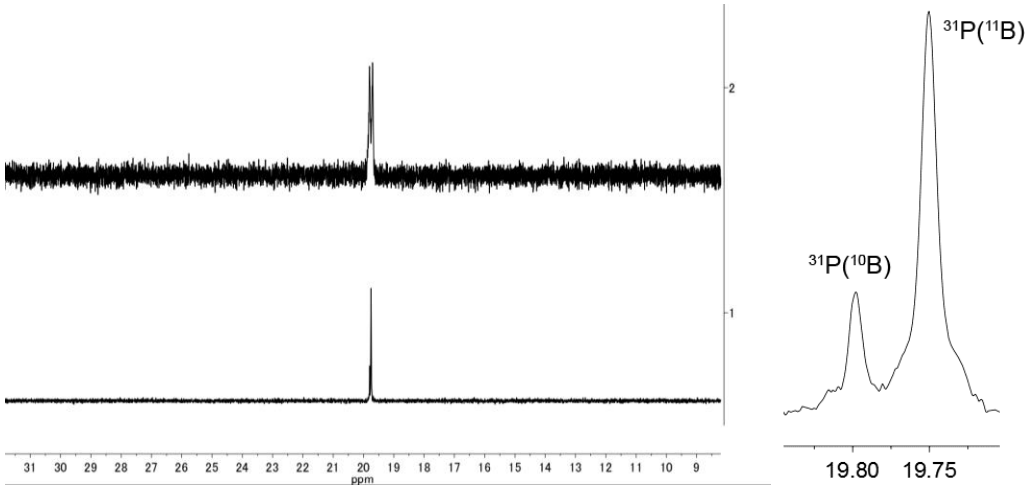


Figure S11 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299 K) spectra of compound **9b**

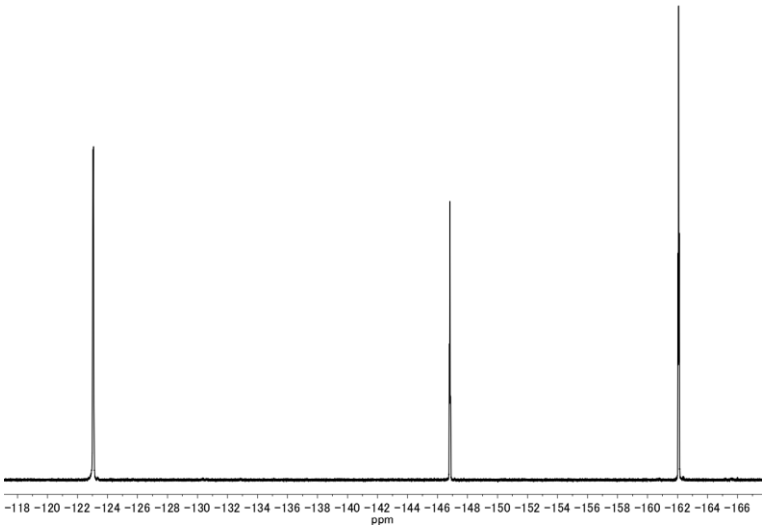


Figure S12 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **9b**

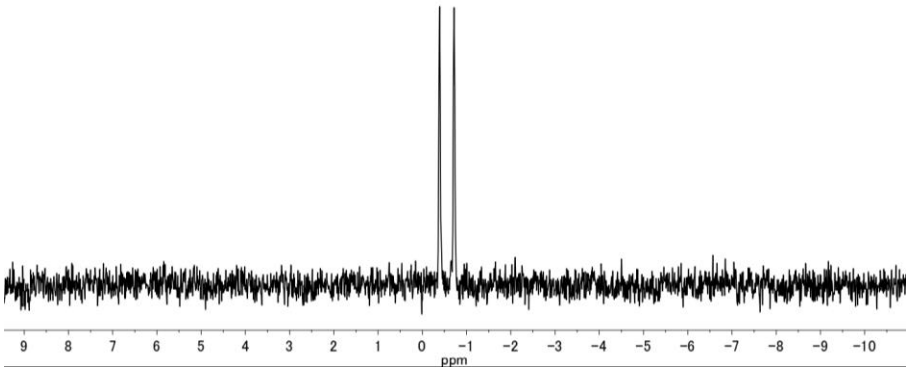


Figure S13 **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **9b**

Crystals suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane into a saturated solution of compound **9b** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 9b (9092.ERK): A colorless plate-like specimen of $C_{35}H_{32}AuBClF_{10}PSi$, approximate dimensions 0.030 mm x 0.090 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a monoclinic unit cell yielded a total of 12002 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 6700 were independent (average redundancy 1.791, completeness = 98.6%, R_{int} = 2.75%, R_{sig} = 3.23%) and 6010 (89.70%) were greater than $2\sigma(F^2)$. The final cell constants of a = 12.6704(2) Å, b = 14.3614(2) Å, c = 21.8280(3) Å, β = 103.7170(10)°, volume = 3858.64(10) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6440 and 0.8890. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{35}H_{32}AuBClF_{10}PSi$. The final anisotropic full-matrix least-squares refinement on F^2 with 460 variables converged at R1 = 3.35%, for the observed data and wR2 = 9.14% for all data. The goodness-of-fit was 1.043. The largest peak in the final difference electron density synthesis was 0.711 e^-/Å^3 and the largest hole was -1.662 e^-/Å^3 with an RMS deviation of 0.112 e^-/Å^3. On the basis of the final model, the calculated density was 1.627 g/cm^3 and F(000), 1848 e^-.

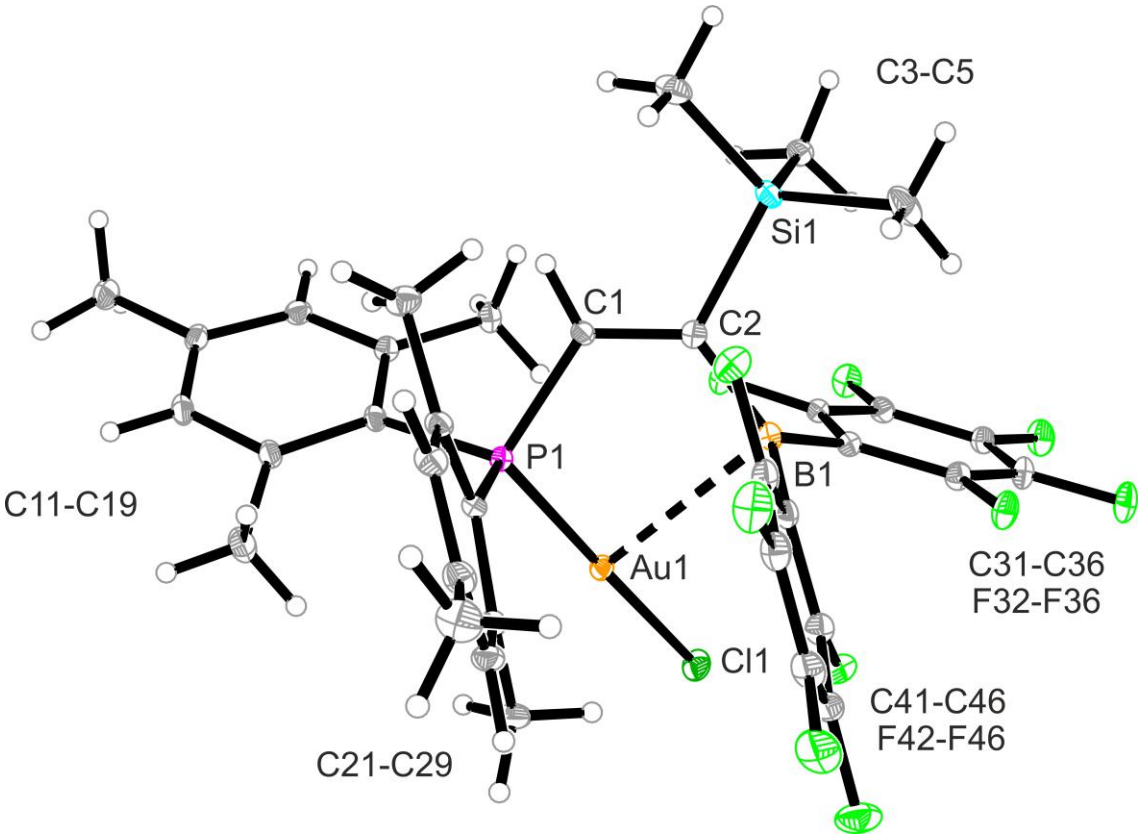
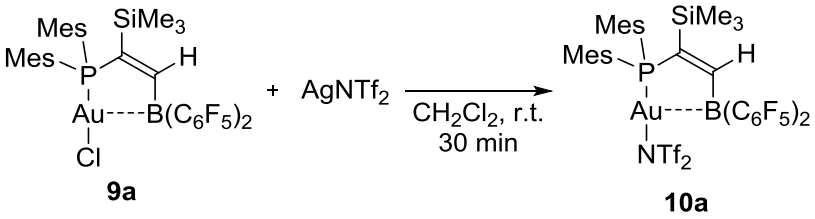


Figure S14

(Thermal ellipsoids are shown with 15% probability)

Preparation of compound 10a:



Scheme S3

A mixture of compound **9a** (94 mg, 0.10 mmol) and $AgNTf_2$ (39 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was stirred for 1 hour at room temperature. After removal of generated AgCl with Celite, all volatiles were removed *in vacuo* and *n*-pentane (2 mL) was added and the mixture stirred for 10 minutes. The white precipitate of the resulting suspension was collected, washed with *n*-pentane (2 mL × 2) and dried *in vacuo* to give compound **10a** as a pale yellow powder (103 mg, 0.087 mmol, 87%).

Elemental Analysis calcd for $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$ (1189.60 g/mol): C, 37.36; H, 2.71; N, 1.18. Found: C, 37.55; H, 2.72; N, 1.09.

^{1}H NMR (600 MHz, CD_2Cl_2, 273 K): δ = 7.31 (dm, $^{3}J_{PH}$ = 92.7 Hz, 1H, BCH=), 6.89 (m, 4H, *m*-Mes), 2.40 (br, 12H, *o*-Me^{Mes}), 2.31 (s, 6H, *p*-Me^{Mes}), 0.04 (s, $^{2}J_{SiH}$ = 6.2 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 273 K): δ = 174.0 (br, BC=), 147.8 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 145.0 (d, $^{1}J_{PC}$ = 25.0 Hz, PC=), 144.1 (dm, $^{1}J_{FC}$ ~ 260 Hz, C_6F_5), 143.4 (d, $^{4}J_{PC}$ = 2.2 Hz, *p*-Mes), 141.9 (d, $^{2}J_{PC}$ = 10.3 Hz, *o*-Mes), 137.4 (dm, $^{1}J_{FC}$ ~ 259 Hz, C_6F_5), 131.8 (d, $^{3}J_{PC}$ = 9.7 Hz, *m*-Mes), 122.8 (d, $^{1}J_{PC}$ = 60.0 Hz, *i*-Mes), 119.6 (q, $^{1}J_{FC}$ ~ 323 Hz, CF_3), 113.2 (br, C_6F_5), 24.7 (d, $^{3}J_{PC}$ = 9.4 Hz, *o*-Me^{Mes}), 20.8 (*p*-Me^{Mes}), 0.43 ($SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 273 K): δ = 51.0 ($\nu_{1/2}$ ~ 1000 Hz).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 273 K): δ = 51.0 ($\nu_{1/2}$ ~ 1000 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 273 K): δ = 32.9 (d, $^{3}J_{PH}$ ~ 93 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 273 K): δ = 33.0102 (^{31}P(^{10}B), 22 mol%), 32.9335 (^{31}P(^{11}B), 78 mol%), [$\Delta^{10/11}$B(^{31}P) = -76.7 ppb].

^{19}F NMR (564 MHz, CD_2Cl_2, 273 K): δ = -73.1 (s, 6F, CF_3), -123.5 (m, 4F, *o*-C_6F_5), -147.9 (m, 2F, *p*-C_6F_5), -162.0 (m, 4F, *m*-C_6F_5), [$\Delta\delta^{19}F_{m,p}$ = 14.0].

^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 273 K): δ = 1.1 (d, $^{2}J_{PSi}$ = 14.5 Hz).

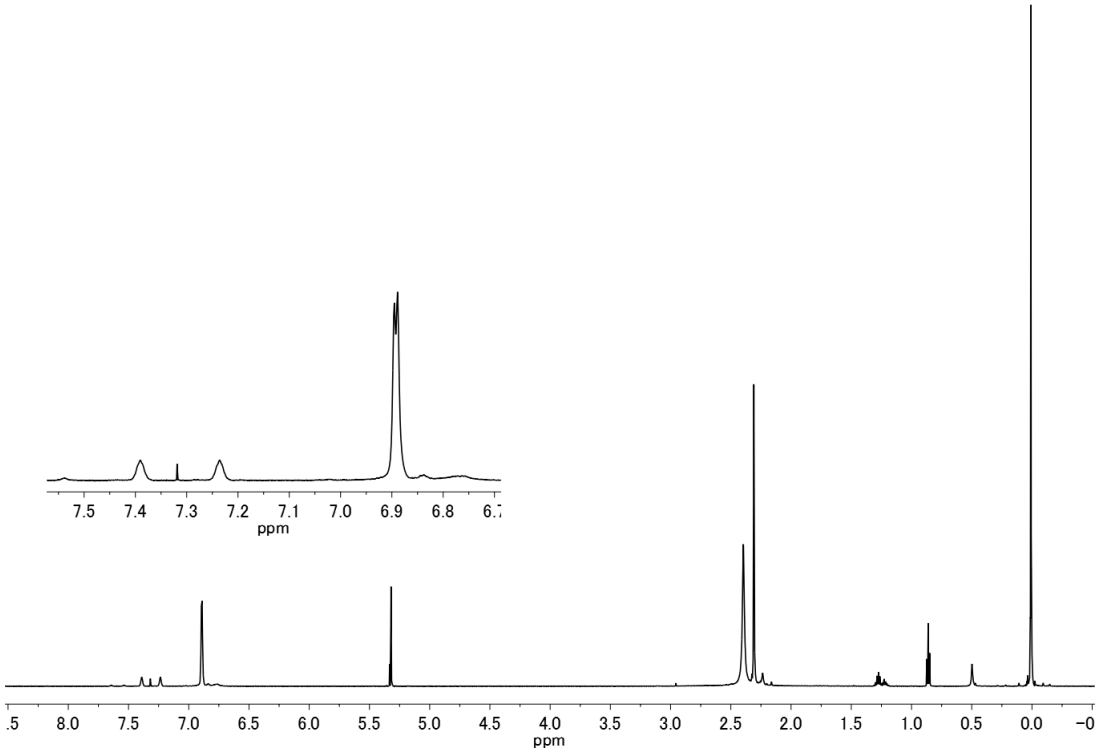


Figure S15 **^{1}H NMR** (600 MHz, CD_2Cl_2, 273 K) spectrum of compound **10a**

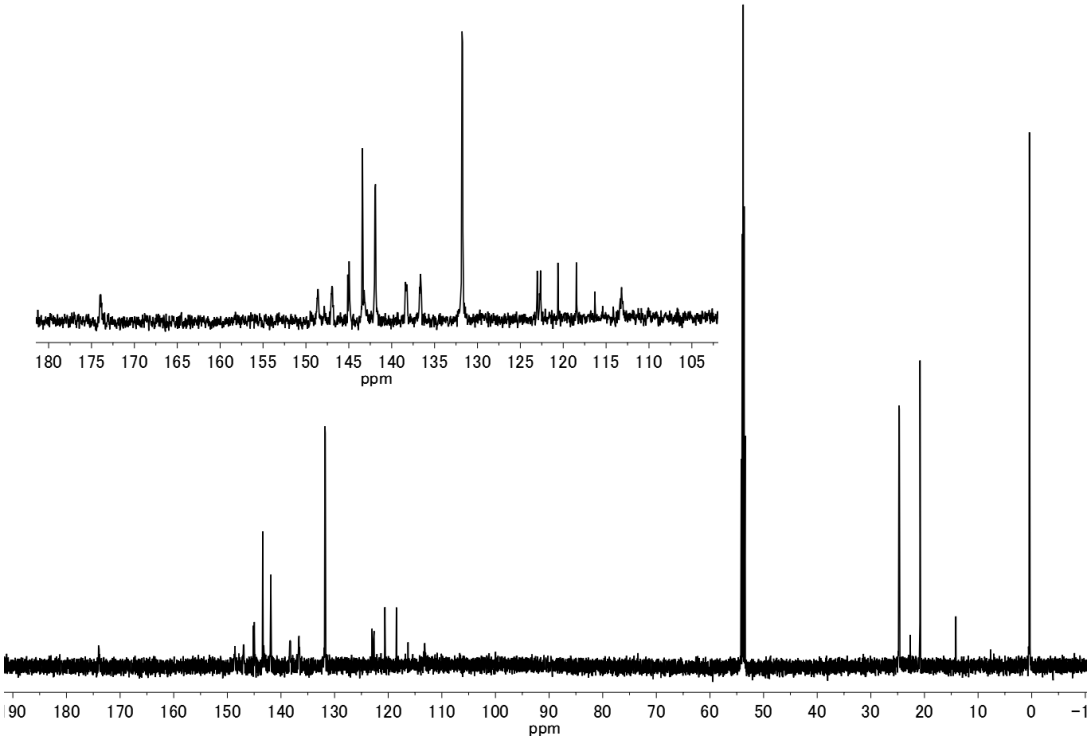


Figure S16 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 273 K) spectrum of compound **10a**

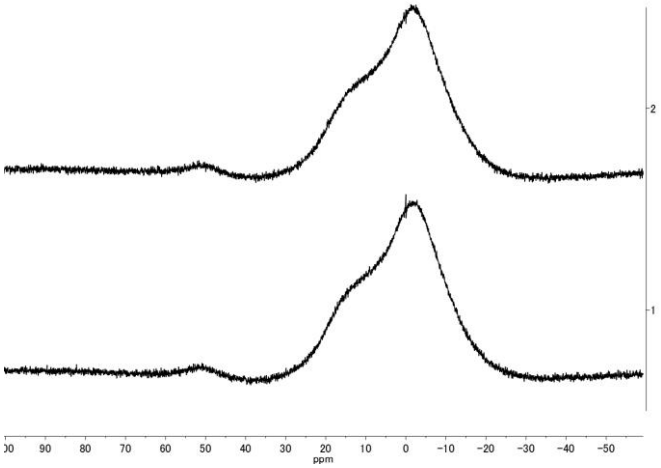


Figure S17 (1) **$^{11}B\{^{1}H\}$** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 273 K) spectra of compound **10a**

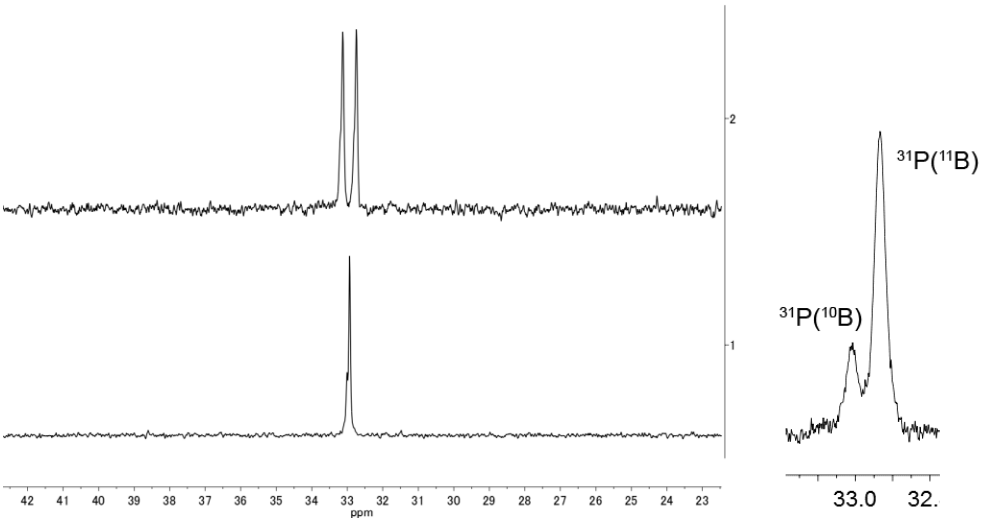


Figure S18 (1) **$^{31}P\{^{1}H\}$** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 273 K) spectra of compound **10a**

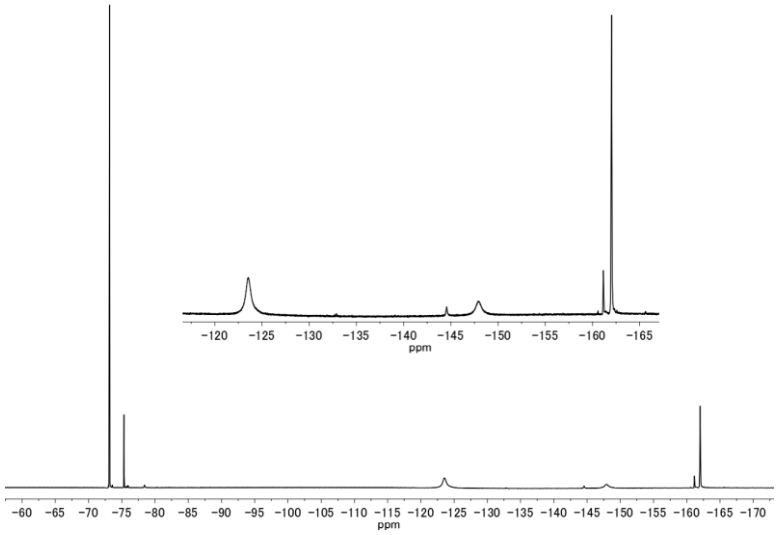


Figure S19 **^{19}F NMR** (564 MHz, CD_2Cl_2, 273 K) spectrum of compound **10a**

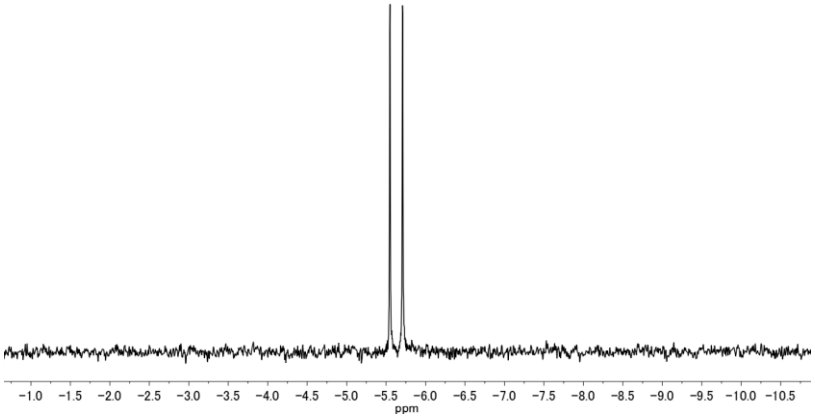


Figure S20 **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 273 K) spectrum of compound **10a**

Crystals suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane into a saturated solution of compound **10a** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 10a (9204.ERK): A yellow prism-like specimen of $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$, approximate dimensions 0.050 mm x 0.070 mm x 0.100 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. The integration of the data using a triclinic unit cell yielded a total of 11394 reflections to a maximum θ angle of 25.00° (0.84 Å resolution), of which 7690 were independent (average redundancy 1.482, completeness = 98.4%, R_{int} = 3.32%, R_{sig} = 3.87%) and 7344 (95.50%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.6920(2) Å, b = 13.3940(3) Å, c = 18.8313(4) Å, α = 71.7140(10)°, β = 82.1690(10)°, γ = 73.107(2)°, volume = 2218.24(9) Å^3, are based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7160 and 0.8410. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *P*-1, with Z = 2 for the formula unit, $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 642 variables converged at R1 = 4.78%, for the observed data and wR2 = 13.17% for all data. The goodness-of-fit was 1.080. The largest peak in the final difference electron density synthesis was 0.920 e$^-$/Å^3 and the largest hole was -4.453 e$^-$/Å^3 with an RMS deviation of 0.173 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.781 g/cm^3 and F(000), 1164 e$^-$.

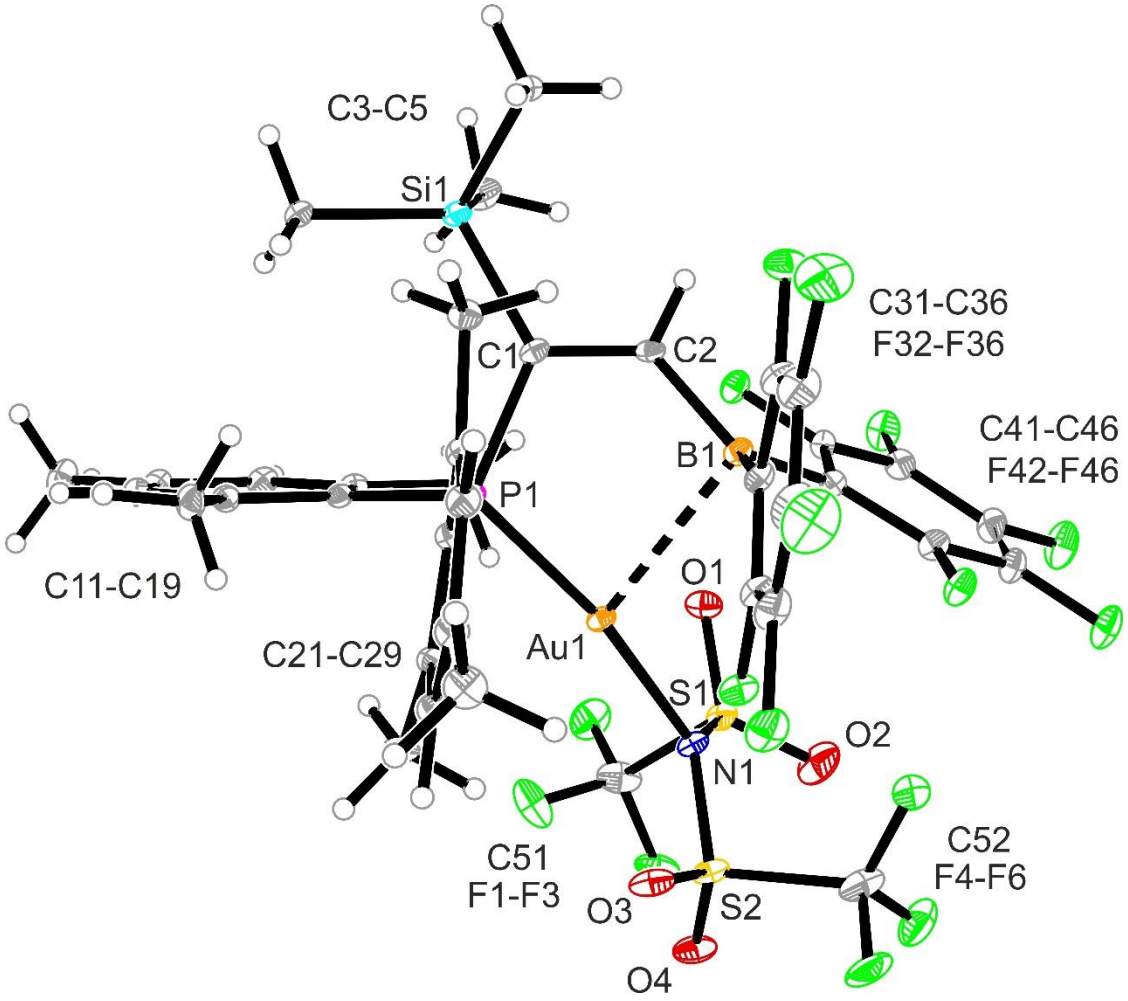
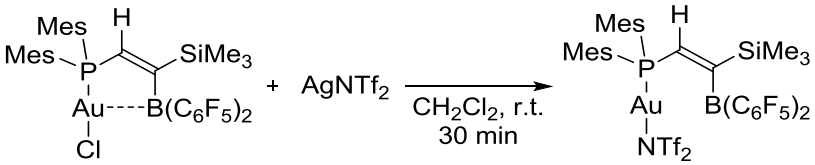


Figure S21

(Thermal ellipsoids are shown with 15% probability)

Preparation of compound 10b:



Scheme S4

A mixture of compound **9b** (94 mg, 0.10 mmol) and $AgNTf_2$ (39 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) was stirred for 1 hour at room temperature. After removal of the generated AgCl with Celite, all volatiles were removed *in vacuo* and *n*-pentane (2 mL) was added and stirred for 10 minutes. The white precipitate of the resulting suspension was collected, washed with *n*-pentane (2 mL × 2) and dried *in vacuo* to give compound **10b** as a white powder (96 mg, 0.081 mmol, 81%).

Elemental Analysis calcd for $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$ (1189.60 g/mol): C, 37.36; H, 2.71; N, 1.18. Found: C, 37.51; H, 2.75; N, 1.26.

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.06 (dm, $^{2}J_{PH}$ = 25.8 Hz, 1H, PCH=), 6.90 (m, 4H, *m*-Mes), 2.34 (s, 12H, *o*-Me^{Mes}), 2.31 (s, 6H, *p*-Me^{Mes}), 0.10 (s, $^{2}J_{SiH}$ = 6.4 Hz, 9H, $SiMe_3$).

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 299 K): δ = 174.1 (br, BC=), 148.9 (dm, $^{1}J_{FC}$ ~ 250 Hz, C_6F_5), 145.1 (dm, $^{1}J_{FC}$ ~ 255 Hz, C_6F_5), 142.8 (d, $^{4}J_{PC}$ = 2.7 Hz, *p*-Mes), 142.0 (d, $^{2}J_{PC}$ = 10.3 Hz, *o*-Mes), 137.8 (dm, $^{1}J_{FC}$ ~ 257 Hz, C_6F_5), 137.0 (d, $^{1}J_{PC}$ = 51.9 Hz, PCH=), 132.1 (d, $^{3}J_{PC}$ = 9.2 Hz, *m*-Mes), 124.0 (d, $^{1}J_{PC}$ = 59.8 Hz, *i*-Mes), 119.7 (q, $^{1}J_{FC}$ ~ 324 Hz, CF_3), 112.7 (br, C_6F_5), 24.4 (d, $^{3}J_{PC}$ = 9.2 Hz, *o*-Me^{Mes}), 20.9 (*p*-Me^{Mes}), -0.7 ($SiMe_3$).

^{11}B NMR (192 MHz, CD_2Cl_2, 299 K): δ = 59.6 ($\nu_{1/2}$ ~ 1700 Hz).

^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 299 K): δ = 59.6 ($\nu_{1/2}$ ~ 1700 Hz).

^{31}P NMR (243 MHz, CD_2Cl_2, 299 K): δ = 5.2 (d, $^{2}J_{PH}$ ~ 26 Hz).

^{31}P{^{1}H} NMR (243 MHz, CD_2Cl_2, 299 K): δ = 5.2 ($\nu_{1/2}$ ~ 10 Hz).

^{19}F NMR (564 MHz, CD_2Cl_2, 299 K): δ = -75.2 (s, 6F, CF_3), -124.1 (m, 4F, *o*-C_6F_5), -145.3 (m, 2F, *p*-C_6F_5), -161.3 (m, 4F, *m*-C_6F_5), [$\Delta\delta\ ^{19}F_{m,\,p}$ = 16.0].

^{29}Si{^{1}H} DEPT (99 MHz, CD_2Cl_2, 299 K): δ = 1.3 (d, $^{3}J_{PSi}$ = 30.0 Hz).

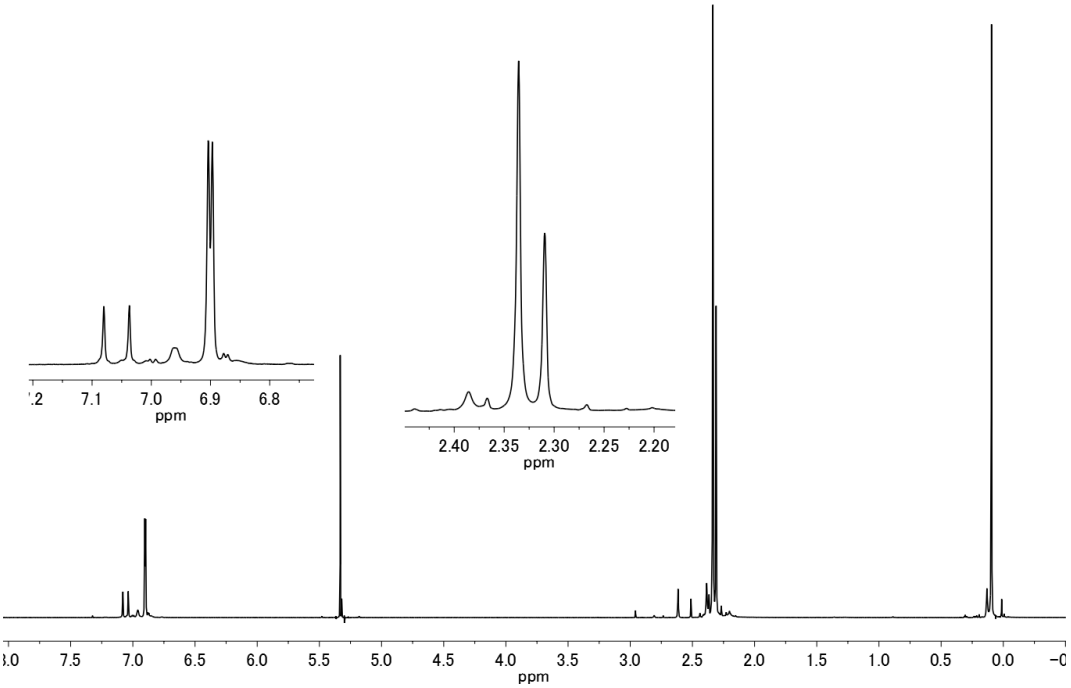


Figure S22 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **10b**

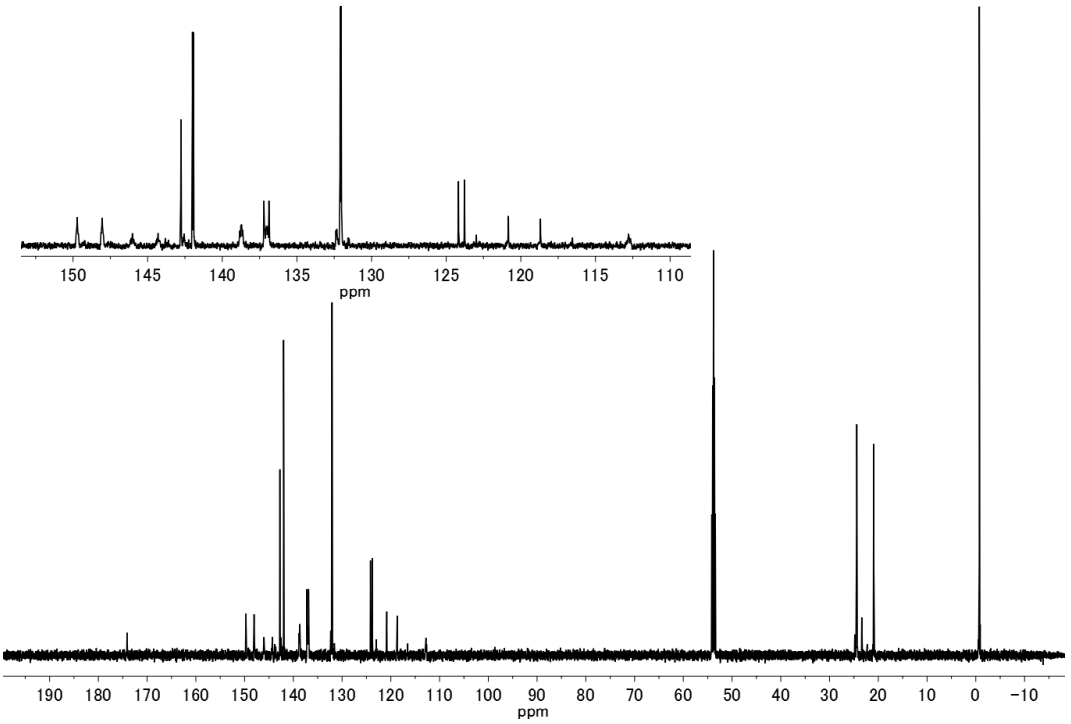


Figure S23 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **10b**

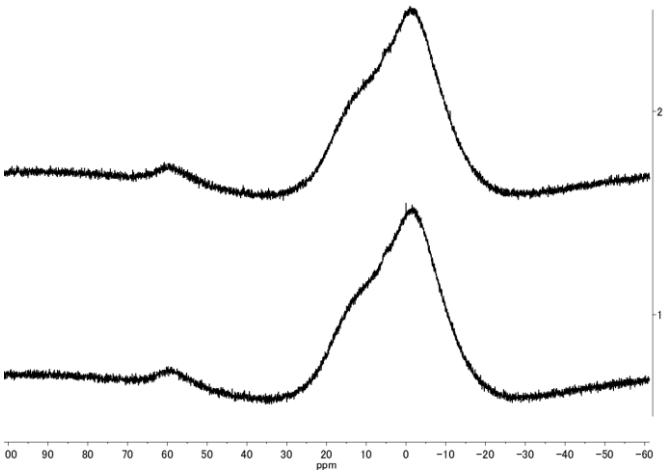


Figure S24 (1) **^{11}B{^{1}H}** and (2) **^{11}B NMR** (192 MHz, CD_2Cl_2, 299 K) spectra of compound **10b**

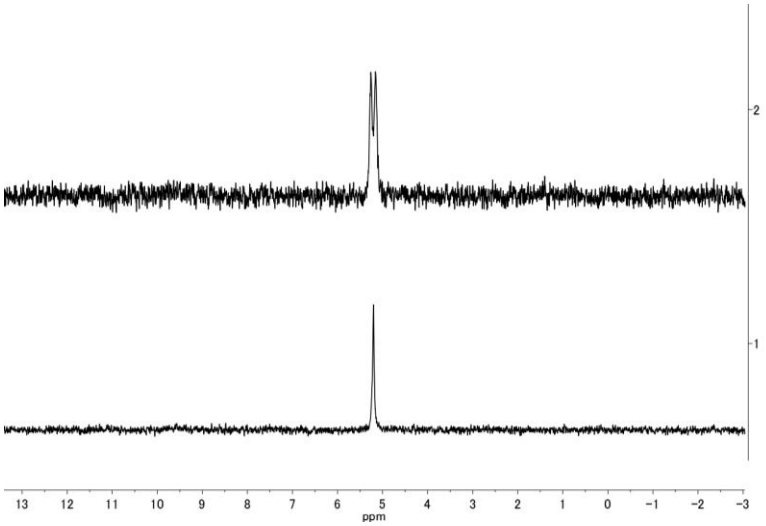


Figure S25 (1) **^{31}P{^{1}H}** and (2) **^{31}P NMR** (243 MHz, CD_2Cl_2, 299 K) spectra of compound **10b**

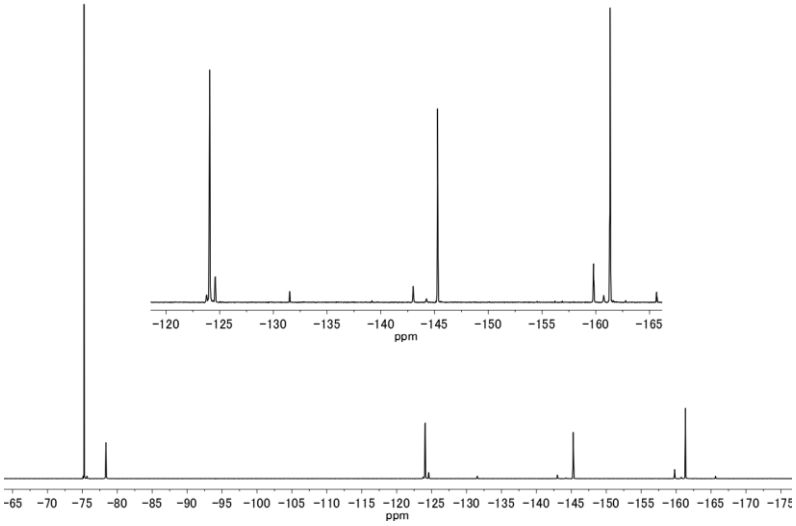


Figure S26 **^{19}F NMR** (564 MHz, CD_2Cl_2, 299 K) spectrum of compound **10b**

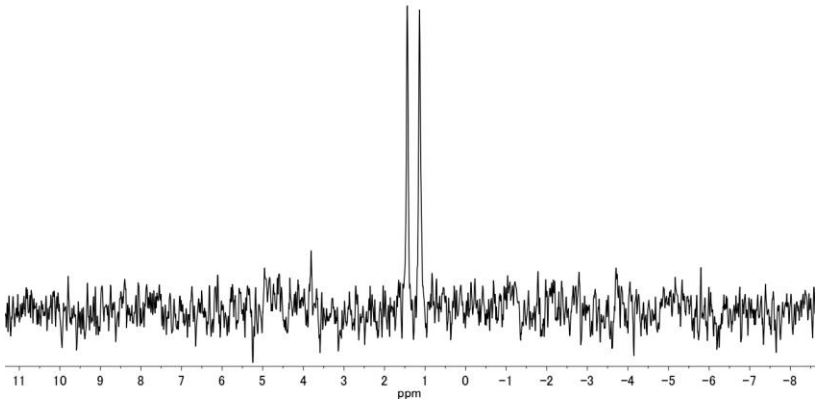


Figure S27 **^{29}Si{^{1}H} DEPT** (99 MHz, CD_2Cl_2, 299 K) spectrum of compound **10b**

Crystals suitable for the X-ray crystal structure analysis were obtained from slow diffusion of pentane into a saturated solution of compound **10b** in CH_2Cl_2 at -35 °C.

X-ray crystal structure analysis of compound 10b (9161.ERK): A colorless prism-like specimen of $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$, approximate dimensions 0.078 mm x 0.160 mm x 0.268 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1257 frames were collected. The total exposure time was 5.24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 115238 reflections to a maximum θ angle of 27.20° (0.78 Å resolution), of which 10215 were independent (average redundancy 11.281, completeness = 99.6%, R_{int} = 5.32%, R_{sig} = 2.54%) and 9290 (90.94%) were greater than $2\sigma(F^2)$. The final cell constants of a = 39.0501(18) Å, b = 10.3111(5) Å, c = 23.3236(9) Å, β = 101.2240(10)°, volume = 9211.6(7) Å^3, are based upon the refinement of the XYZ-centroids of 9616 reflections above 20 σ(I) with 5.171° < 2θ < 54.24°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.820. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4580 and 0.7750. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group *C*2/*c*, with Z = 8 for the formula unit, $C_{37}H_{32}AuBF_{16}NO_4PS_2Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 713 variables converged at R1 = 2.82%, for the observed data and wR2 = 5.52% for all data. The goodness-of-fit was 1.171. The largest peak in the final difference electron density synthesis was 0.859 e^-/Å^3 and the largest hole was -1.979 e^-/Å^3 with an RMS deviation of 0.088 e^-/Å^3. On the basis of the final model, the calculated density was 1.716 g/cm^3 and F(000), 4656 e^-.

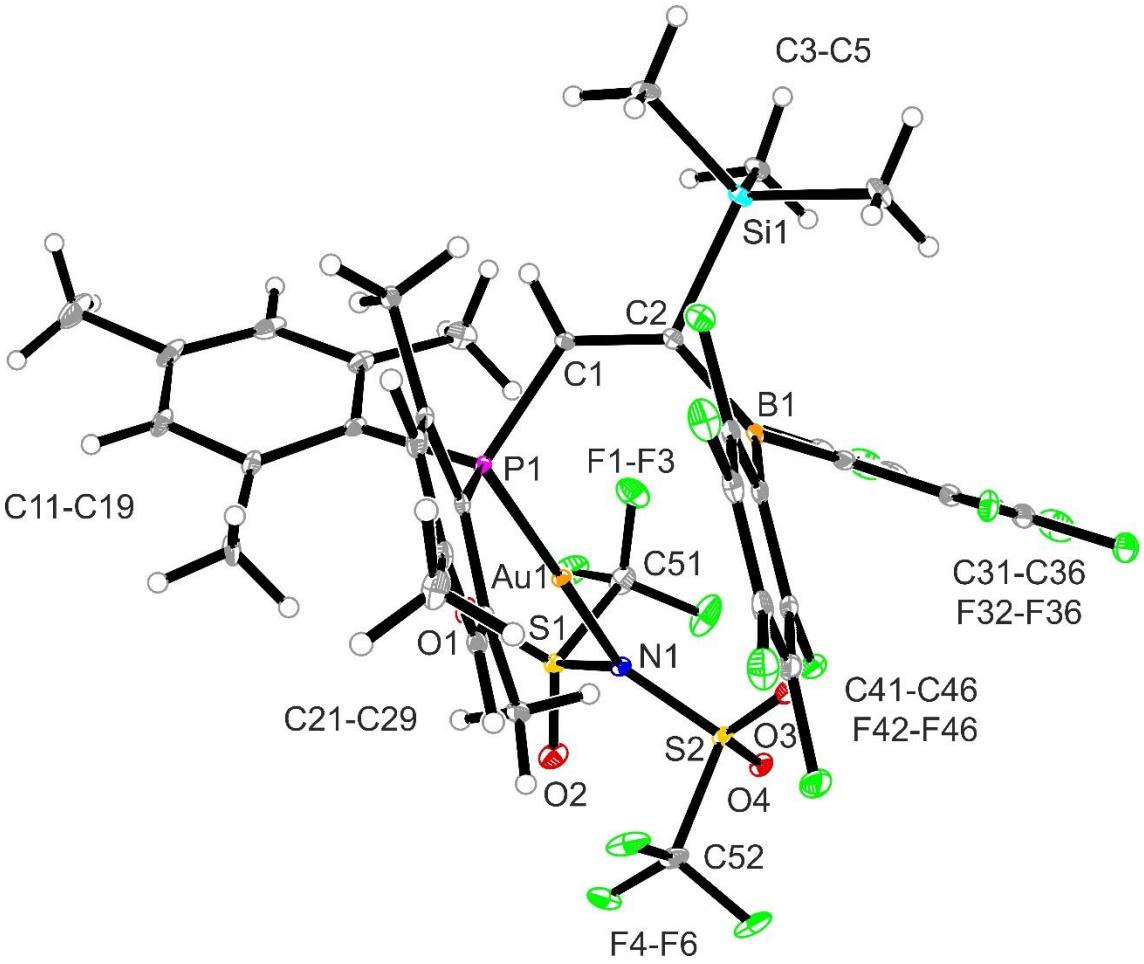
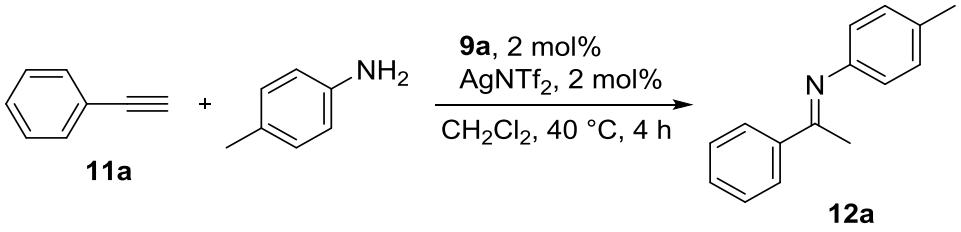


Figure S28

(Thermal ellipsoids are shown with 15% probability)

Catalytic hydroamination reactions.

Preparation of compound 12a:

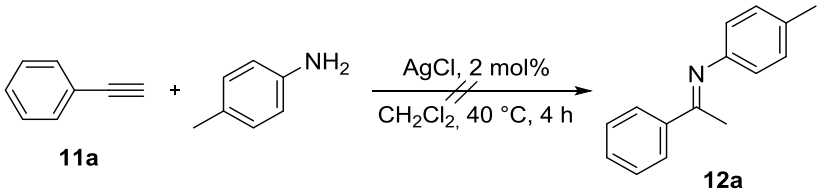


Scheme S5

For the synthesis of compound **12a** a solution of phenylacetylene (102 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compound **9a** (18.8 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (2 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After purification by silica gel column chromatography (pentane/CH_2Cl_2 = 1/1), compound **12a** was obtained as a yellow oil (182 mg, 0.87 mmol, 87%). The NMR data were in good agreement with those given in the literature [C. Reddy V. Reddy, S. Urgaonkar, J. G. Verkade *Org. Lett.* 2005, **7**, 4427].

Preparation of compound 12a, control experiments:

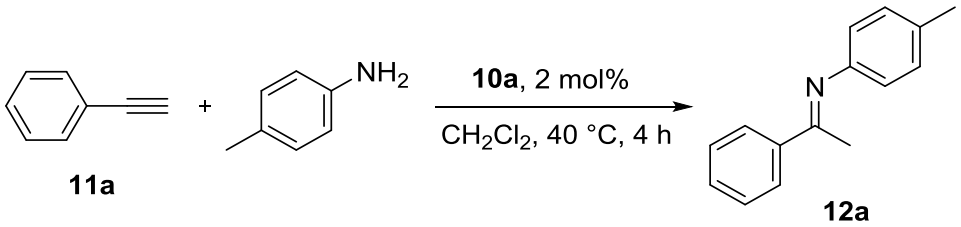
a) Au-free:



Scheme S6

A solution of phenylacetylene (26 mg, 0.25 mmol), *p*-toluidine (27 mg, 0.25 mmol), AgCl (0.7 mg, 0.005 mmol, 2 mol%) in CD_2Cl_2 (0.5 mL) was heated for 4 hours at 40 °C. Then the reaction mixture was characterized by ^{1}H NMR experiments: no conversion was observed.

b) Ag-free with compound **10a**:



Scheme S7

A solution of phenylacetylene (26 mg, 0.25 mmol), *p*-toluidine (27 mg, 0.25 mmol), compound **10a** (6.0 mg; 0.005 mmol, 2 mol%) in CD_2Cl_2 (0.5 mL) was heated for 4 hours at 40 °C. Then the reaction mixture was characterized by ^{1}H NMR experiments: close to complete conversion to the hydroamination product was observed.

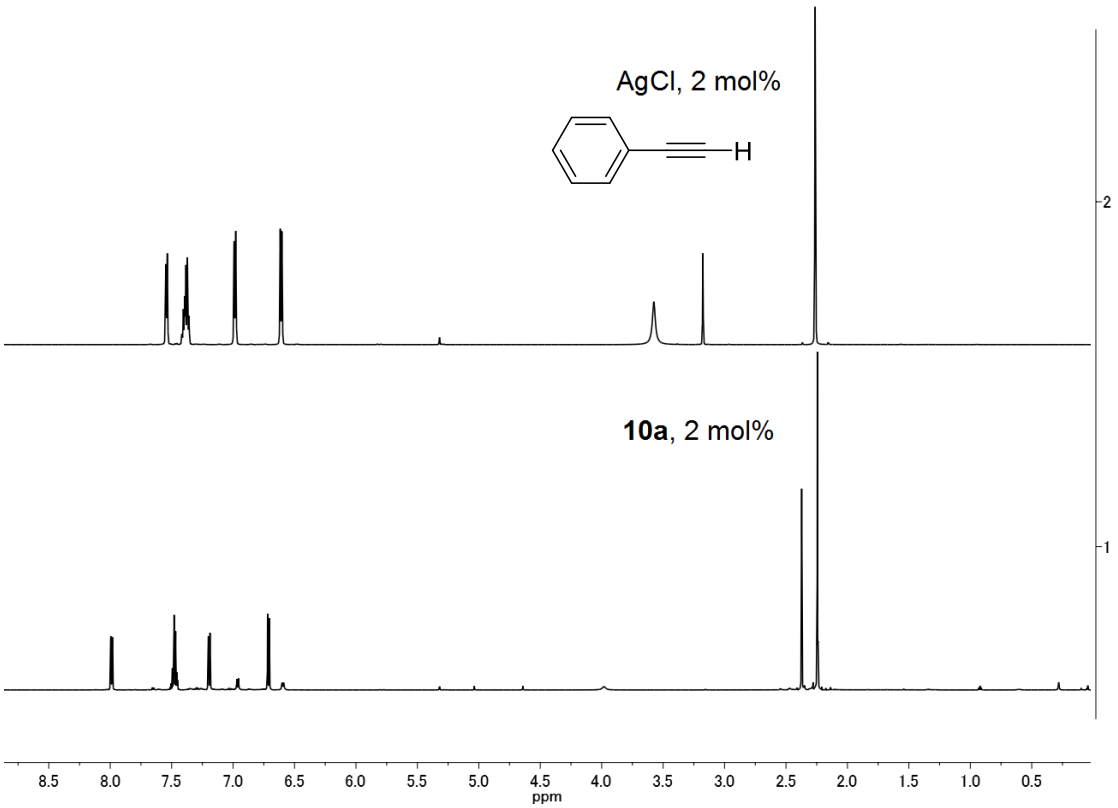
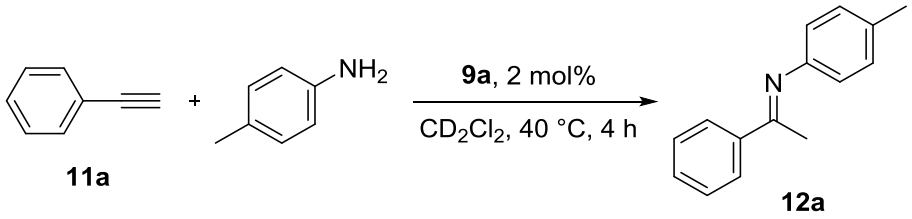


Figure S29 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) hydroamination reaction of phenylacetylene with *p*-toluidine; (1) with 2 mol% of compound **10a**. (2) control reaction with 2 mol% of AgCl.

c) Ag-free reaction with compound **9a**:



Scheme S8

A solution of phenylacetylene (26 mg, 0.25 mmol), *p*-toluidine (27 mg, 0.25 mmol), compound **9a** (4.7 mg; 0.005 mmol, 2 mol%) in CD_2Cl_2 (0.5 mL) was heated for 4 hours at 40 °C. Then the reaction mixture was characterized by ^{1}H NMR experiments: hydroamination product was observed in traces (< 4 mol% yield).

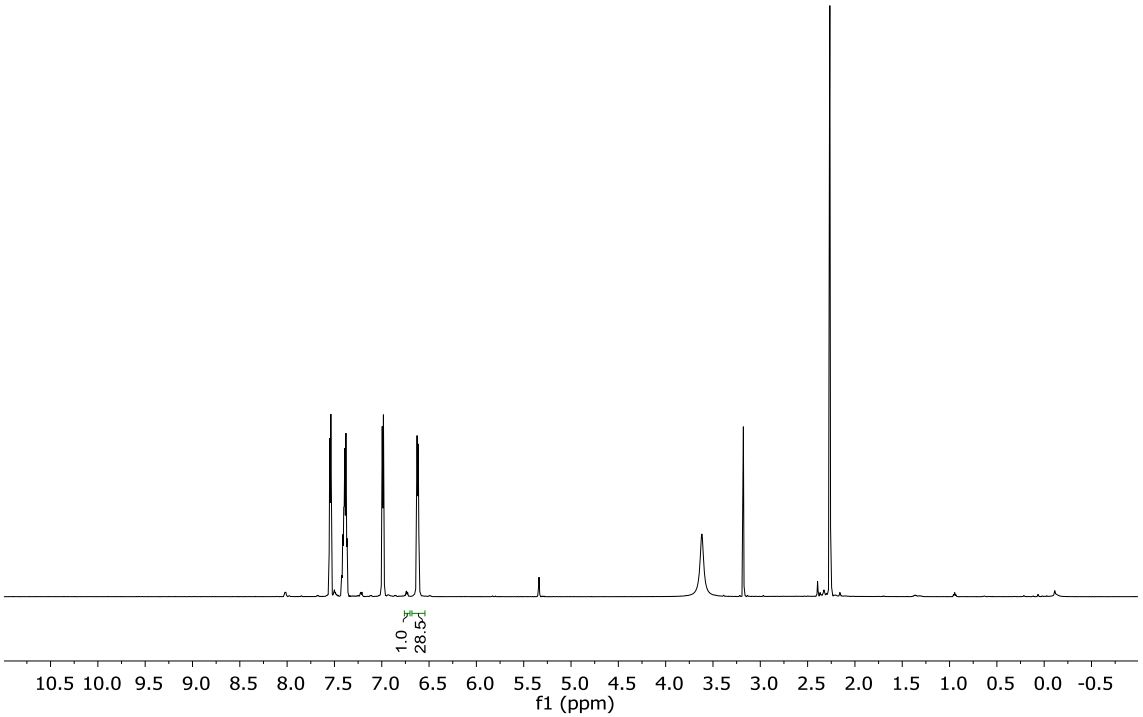
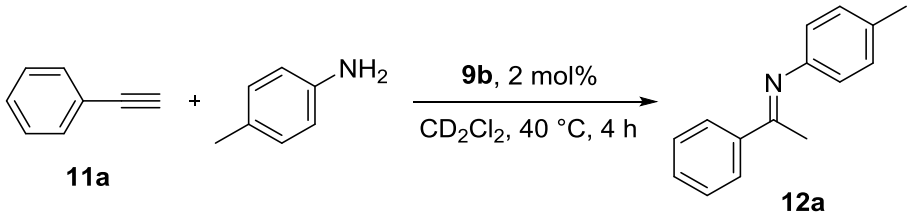


Figure S30 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) hydroamination reaction of phenylacetylene with *p*-toluidine in the presence of 2 mol% of compound **9a** without silver salt.

d) Ag-free reaction with compound **9b**:



Scheme S9

A solution of phenylacetylene (26 mg, 0.25 mmol), *p*-toluidine (27 mg, 0.25 mmol), compound **9b** (4.7 mg; 0.005 mmol, 2 mol%) in CD_2Cl_2 (0.5 mL) was heated for 4 hours at 40 °C. Then the reaction mixture was characterized by ^{1}H NMR experiments: hydroamination product was observed in ca. 9 mol% yield.

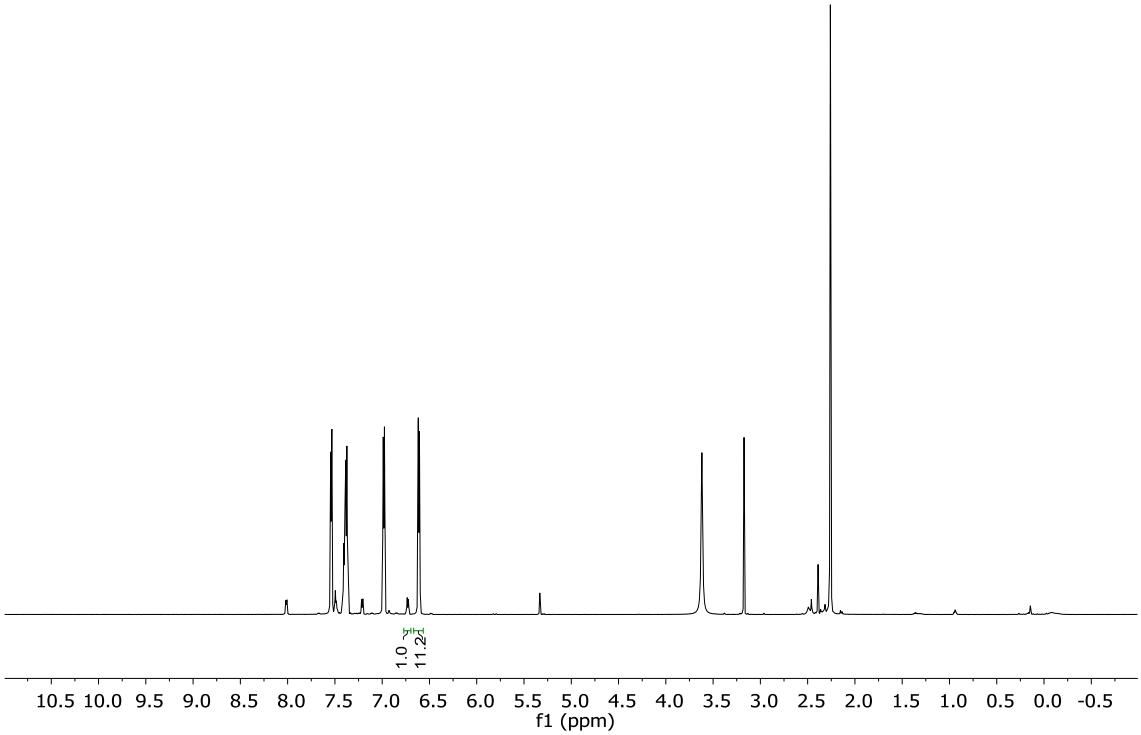
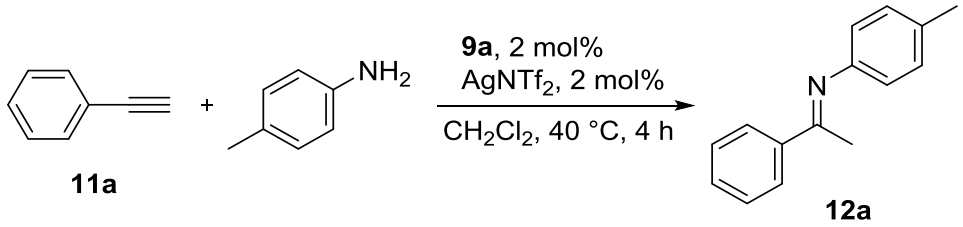


Figure S31 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) hydroamination reaction of phenylacetylene with *p*-toluidine in the presence of 2 mol% of compound **9b** without silver salt.

Preparation of compound 12a (gram scale reaction):

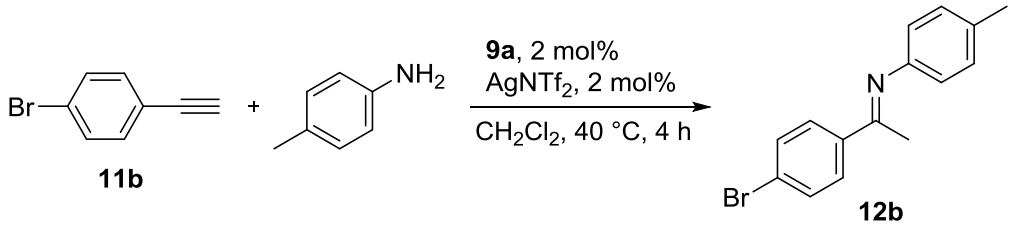


Scheme S10

A solution of phenylacetylene (1 g, 10 mmol), *p*-toluidine (1.1 g, 10 mmol), compound **9a** (188 mg, 0.2 mmol, 2 mol%), and $AgNTf_2$ (77 mg, 0.2 mmol, 2 mol%) in CH_2Cl_2 (20 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo*. After the purification by silica gel column chromatography (pentane/CH_2Cl_2 = 1/1), compound **12a** was obtained as a yellow oil (1.98 g, 0.95 mmol, 95%).

The NMR data were in good agreement with those given in the literature [C. Reddy V. Reddy, S. Urgaonkar, J. G. Verkade *Org. Lett.* **2005**, *7*, 4427].

Preparation of compound 12b:



Scheme S11

A solution of 4-bromoethynylbenzene (**11b**, 181 mg, 1.00 mmol), *p*-toluidine (107 mg, 1.00 mmol), compound **9a** (18.8 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (2 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After the purification by silica gel column chromatography (pentane/CH_2Cl_2 = 1/1), compound **12b** was obtained as a yellow solid (265 mg, 0.92 mmol, 92%).

HRMS: m/z calc. for $C_{15}H_{14}BrN+[H^+]$ 288.0387; found 288.0389

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.84 (m, 2H, Ar), 7.57 (m, 2H, Ar), 7.16 (m, 2H, Ar), 6.69 (m, 2H, Ar), 2.35 (s, 3H, Me^{Tol}), 2.21 (s, 3H, $Me^{N=C}$).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 164.3 (N=C), 148.7 (C^{Tol}), 138.5 (C^{Ar}), 132.8 (C^{Tol}), 131.5 (CH^{Ar}), 129.5 (CH^{Tol}), 128.7 (CH^{Ar}), 124.9 (C^{Ar}), 119.3 (CH^{Tol}), 20.8 (Me^{Tol}), 17.1 ($Me^{N=C}$).

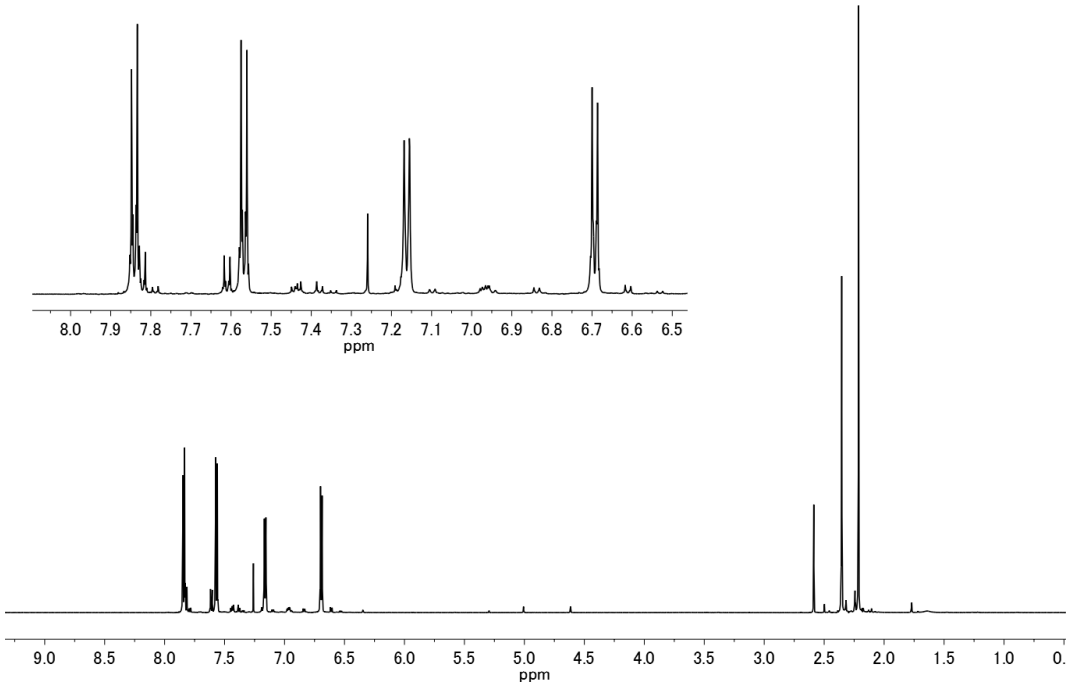


Figure S32 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **12b**

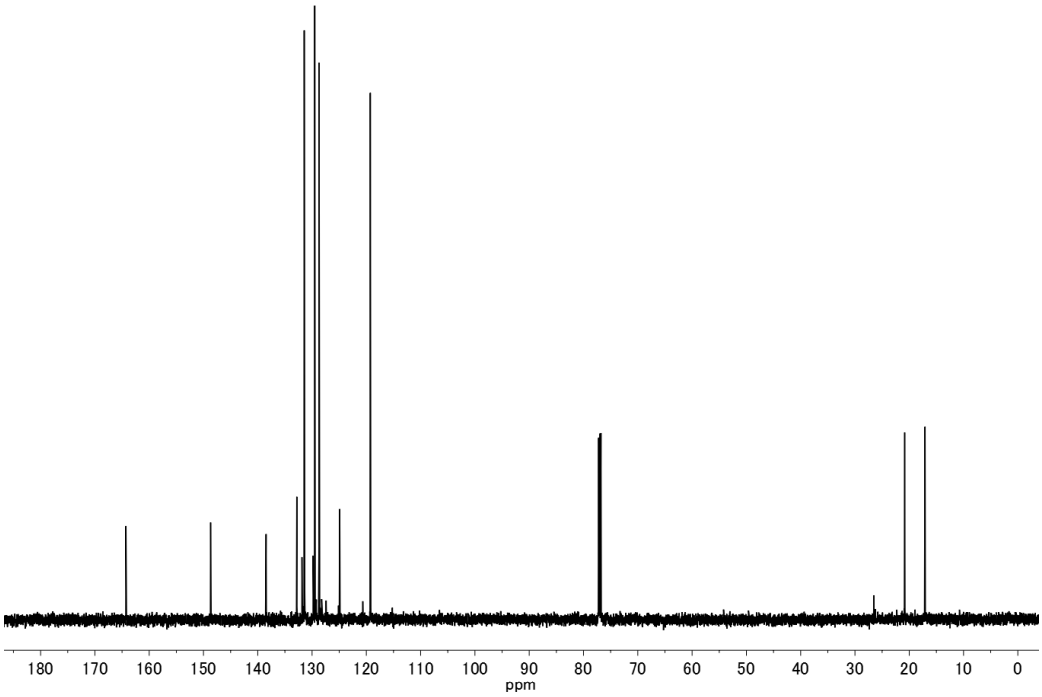
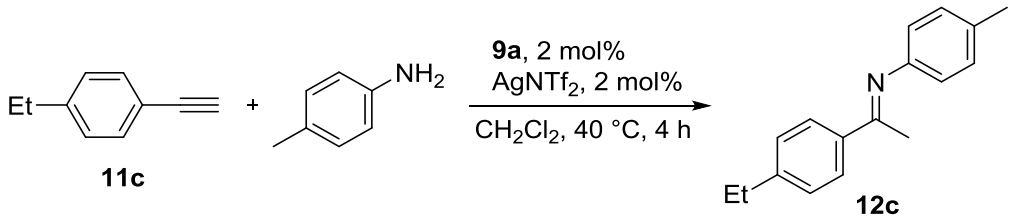


Figure S33 **$^{13}C\{^1H\}$ NMR** (151 MHz, $CDCl_3$, 299 K) spectrum of compound **12b**

Preparation of compound 12c:



Scheme S12

A solution of 4-ethylethynylbenzene (**11c**, 130 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compound **9a** (18.8 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (2 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After the purification by silica gel column chromatography (pentane/CH_2Cl_2 = 1/1), compound **12c** was obtained as a yellow solid (217 mg, 0.92 mmol, 92%).

HRMS: m/z calc. for $C_{17}H_{19}N+[H^+]$ 238.1596; found 238.1594

^{1}H NMR (600 MHz, CD_2Cl_2, 299 K): δ = 7.89 (m, 2H, Ar), 7.30 (m, 2H, Ar), 7.18 (m, 2H, Ar), 6.69 (m, 2H, Ar), 2.73 (q, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2^{Et}), 2.36 (s, 3H, Me^{Tol}), 2.23 (s, 3H, $Me^{N=C}$), 1.29 (t, $^3J_{HH}$ = 7.6 Hz, 2H, Me^{Et}).

$^{13}C\{^1H\}$ NMR (151 MHz, CD_2Cl_2, 299 K): δ = 166.5 (N=C), 149.0 (C^{Tol}), 147.7 (C^{Ar}), 137.3 (C^{Ar}), 133.3 (C^{Tol}), 129.9 (CH^{Tol}), 128.2 (CH^{Ar}), 127.6 (CH^{Ar}), 119.9 (CH^{Tol}), 29.1 (CH_2^{Et}), 20.9 (Me^{Tol}), 17.5 ($Me^{N=C}$), 15.6 (Me^{Et}).

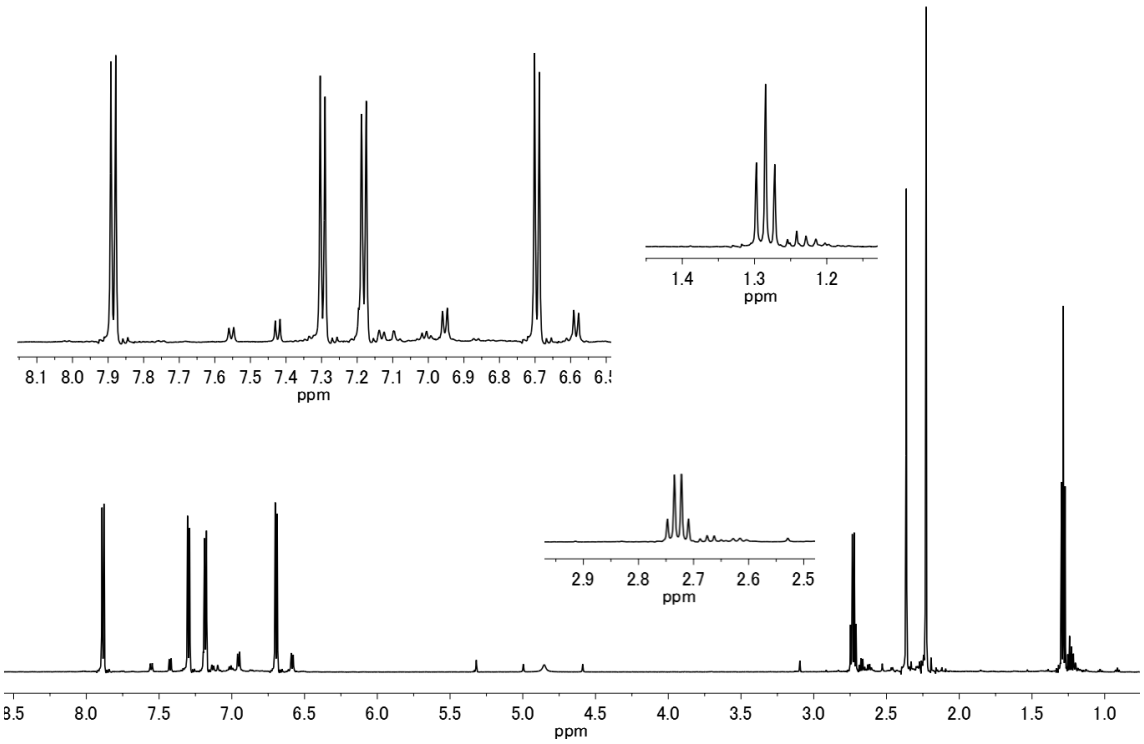


Figure S34 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of compound **12c**

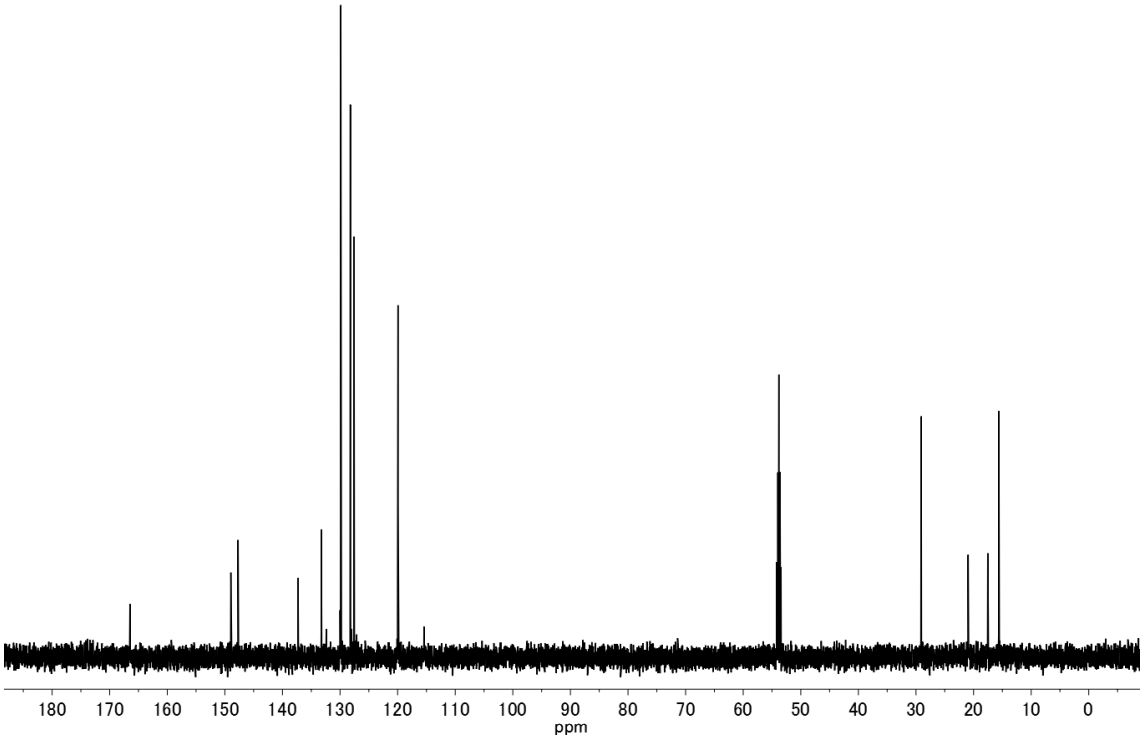
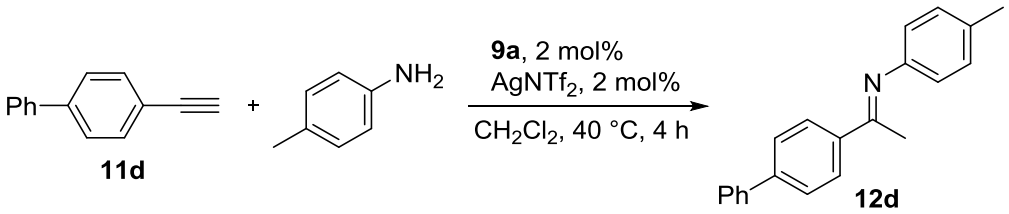


Figure S35 **^{13}C{^{1}H} NMR** (151 MHz, CD_2Cl_2, 299 K) spectrum of compound **12c**

Preparation of compound 12d:



Scheme S13

A solution of 4-phenylethynylbenzene (**11d**, 178 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compound **9a** (18.8 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (2 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After the purification by silica gel column chromatography (pentane/acetone = 4/1), compound **12d** was obtained as a pale yellow solid (265 mg, 0.93 mmol, 93%).

HRMS: m/z calc. for $C_{21}H_{19}N+[H^+]$ 286.1596; found 286.1589

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 8.05 (m, 2H, Ar), 7.69 (m, 2H, Ar), 7.65 (m, 2H, Ar), 7.47 (m, 2H, Ar), 7.39 (m, 1H, Ar), 7.18 (m, 2H, CH^{Tol}), 6.75 (m, 2H, CH^{Tol}), 2.36 (s, 3H, Me^{Tol}), 2.29 (s, 3H, $Me^{N=C}$).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 165.0 (N=C), 149.1 (C^{Tol}), 143.0 (C^{Ar}), 140.4 (C^{Ar}), 138.5 (C^{Ar}), 132.6 (C^{Tol}), 129.5 (CH^{Tol}), 128.8 (CH^{Ar}), 127.7 (CH^{Ar}), 127.6 (CH^{Ar}), 127.1 (CH^{Ar}), 127.0 (CH^{Ar}), 119.4 (CH^{Tol}), 20.9 (Me^{Tol}), 17.3 ($Me^{N=C}$).

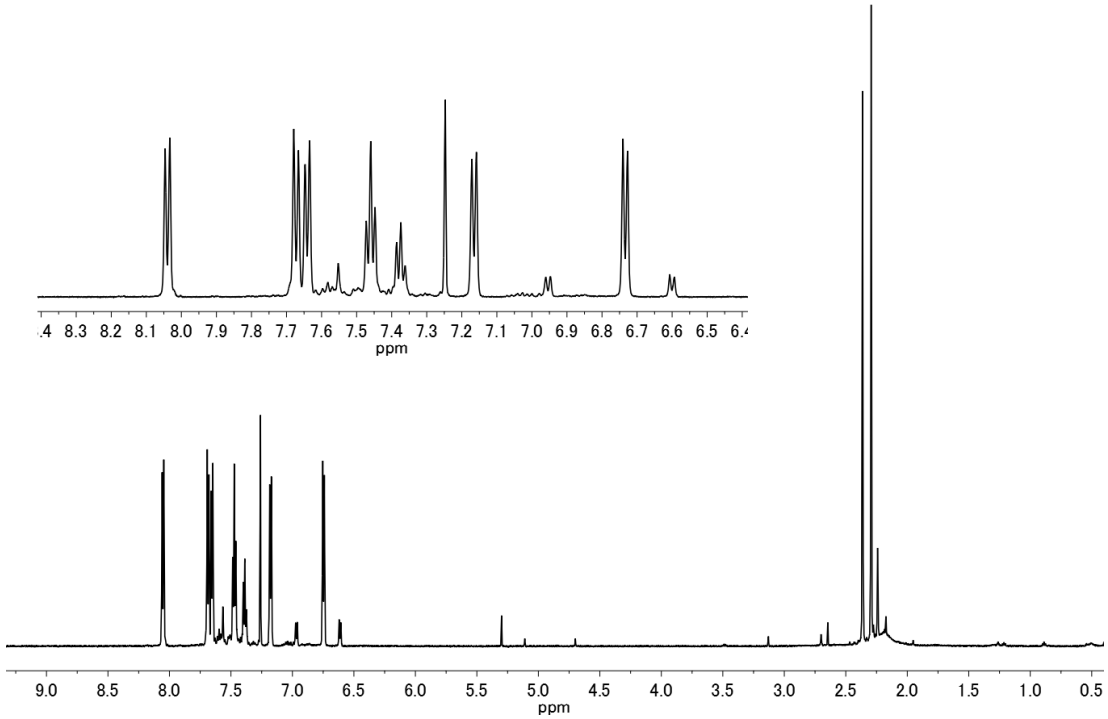


Figure S36 **^{1}H NMR** (600 MHz, $CDCl_3$, 299 K) spectrum of compound **12d**

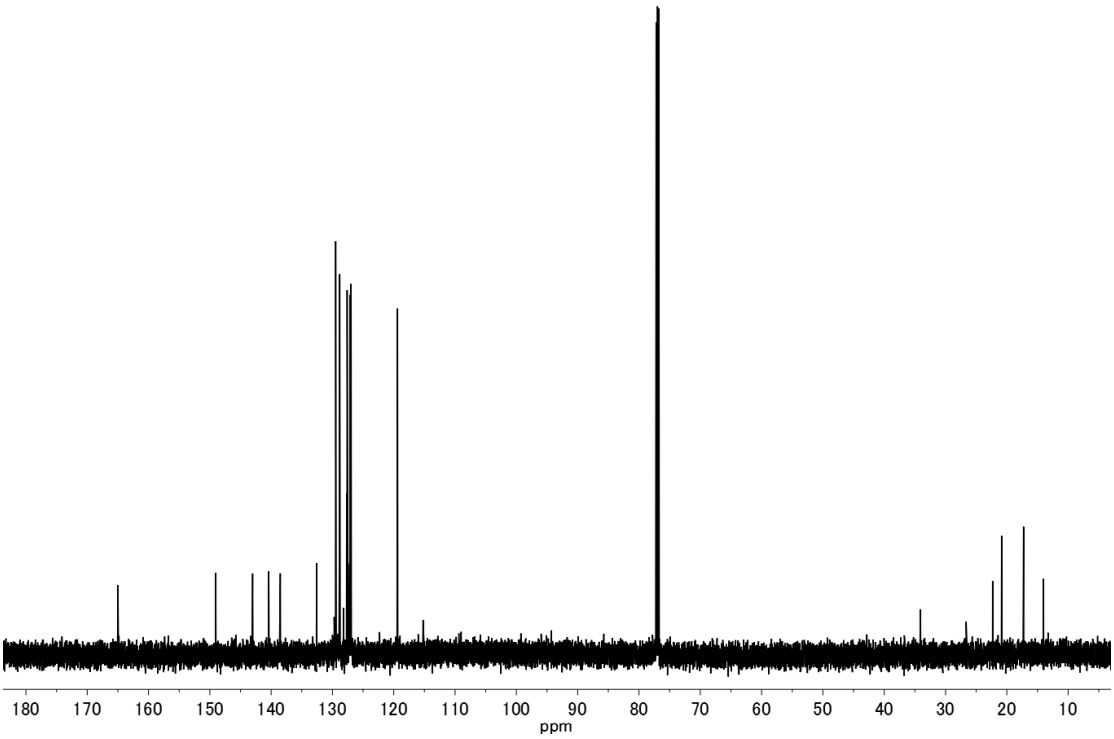
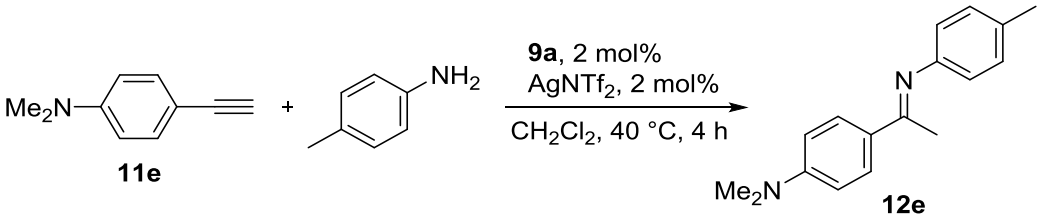


Figure S37 **$^{13}C\{^{1}H\}$ NMR** (151 MHz, $CDCl_3$, 299 K) spectrum of compound **12d**

Preparation of compound 12e:



Scheme S14

A solution of 4-ethynyl-*N*,*N*-dimethylaniline (**11e**, 145 mg, 1.0 mmol), *p*-toluidine (102 mg, 1.0 mmol), comound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After purification by silica gel column chromatography (pentane/acetone = 4/1), compound **12e** was obtained as an orange powder (236 mg, 0.94 mmol, 94% isolated).

HRMS: m/z calc. for $C_{17}H_{20}N_2$+[H^+] 253.1705; found 253.1708

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.88 (m, 2H, CH^{Ar}), 7.13 (m, 2H, CH^{Tol}), 6.72 (m, 2H, CH^{Ar}), 6.69 (m, 2H, CH^{Tol}), 3.03 (s, 6H, NMe_2), 3.34 (s, 3H, Me^{Tol}), 2.17 (s, 3H, $Me^{N=C}$).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 299 K): δ = 164.5 (N=C), 151.9 (C^{Ar}), 149.7 (C^{Tol}), 131.9 (C^{Tol}), 129.4 (CH^{Tol}), 128.5 (CH^{Ar}), 127.5 (C^{Ar}), 119.8 (CH^{Tol}), 111.3 (CH^{Ar}), 40.2 (NMe_2), 20.8 (Me^{Tol}), 16.8 ($Me^{N=C}$).

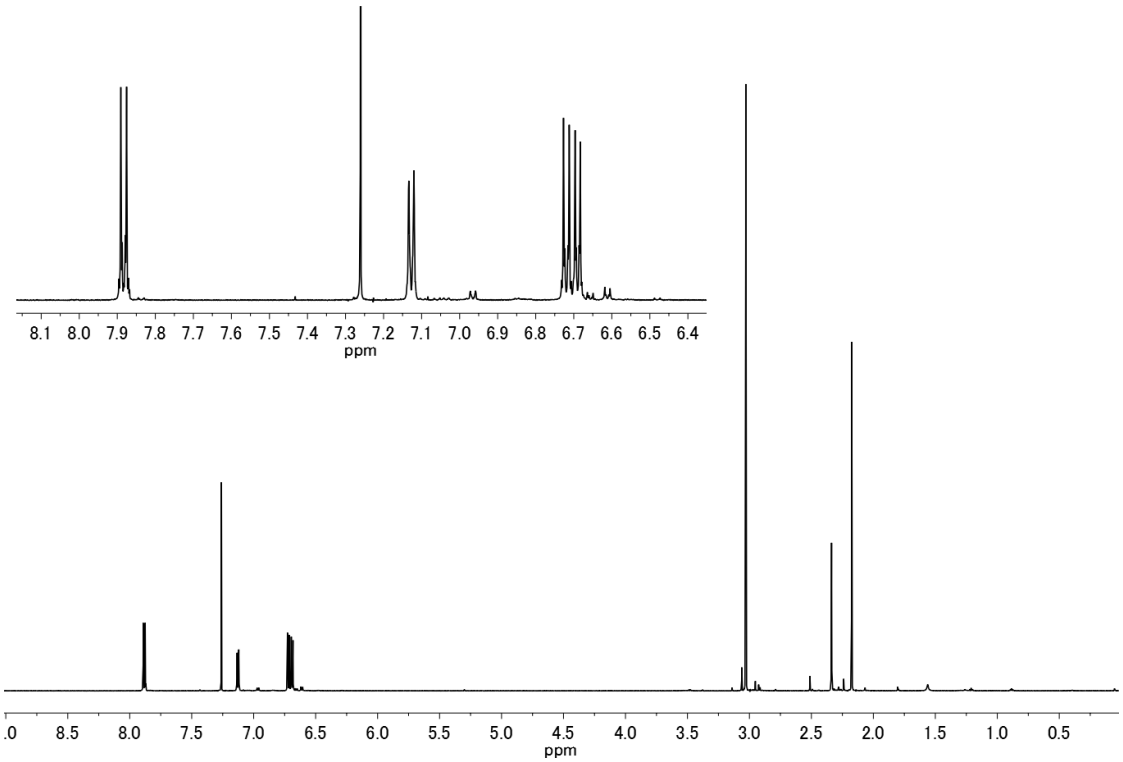


Figure S38 **^{1}H NMR** (600 MHz, $CDCl_3$, 299 K) spectrum of compound **12e**

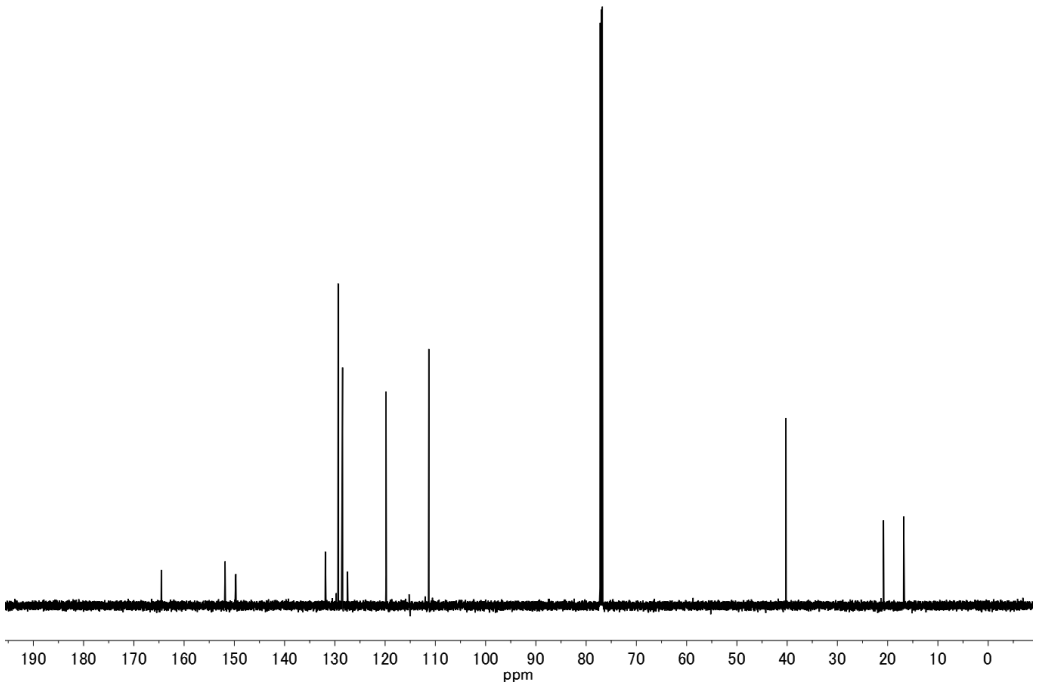
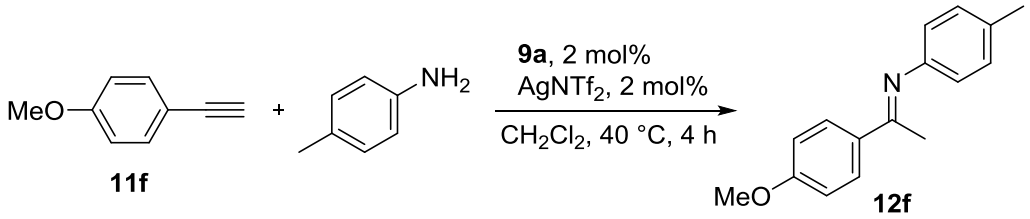


Figure S39 **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 299 K) spectrum of compound **12e**

Preparation of compound 12f:

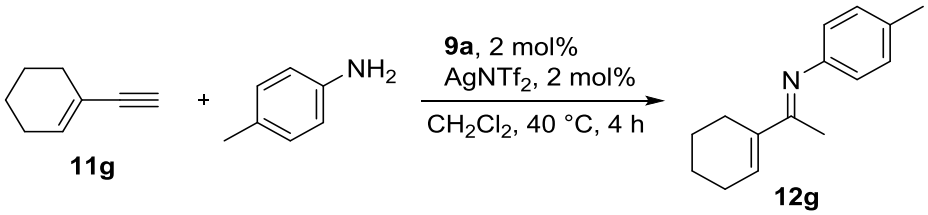


Scheme S15

A solution of 4-methoxyphenylacetylene (**11f**, 132 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo*. After purification by silica gel column chromatography (pentane/acetone = 4/1), compound **12f** was obtained as an yellow powder (208 mg, 0.87 mmol, 87% isolated). The NMR data were in good agreement with those given in the literature. [B. Li, C. B. Bheeter, C. Darcel, P. H. Dixneuf, *ACS Catal.* **2011**, *1*, 1221–1224].

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.94 (d, 2H, Ar), 7.15 (d, 2H, Ar), 6.95 (d, 2H, Ar), 6.70 (d, 2H, Ar), 3.86 (s, 6H, OMe), 2.35 (s, 3H, Me^{Tol}), 2.21 (s, 3H, $Me^{N=C}$).

Preparation of compound 12g:



Scheme S16

A solution of 1-ethynylcyclohexene (**11g**, 106 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compund **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After purification by silica gel column chromatography (pentane/acetone = 9/1), compound **12g** was obtained as an orange oil (185 mg, 0.87 mmol, 87% isolated).

HRMS: m/z calc. for $C_{15}H_{19}N+[H^+]$ 214.1596; found 214.1600

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.09 (m, 2H, CH^{Tol}), 6.58 (m, 2H, CH^{Tol}), 6.51 (m, 1H, CH^{Hex}), 2.44 (m, 2H, CH_2^{Hex}), 2.31 (s, 3H, CH_3^{Tol}), 2.25 (m, 2H, CH_2^{Hex}), 1.92 (s, 3H, $Me^{N=C}$), 1.70 (s, 2H, CH_2^{Hex}), 1.65 (s, 2H, CH_2^{Hex}).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 166.6 (N=C), 149.5 (C^{Tol}), 139.5 (C^{Hex}), 133.4 (CH^{Hex}), 132.0 (C^{Tol}), 129.3 (CH^{Tol}), 119.3 (CH^{Tol}), 26.2 (CH_2^{Hex}), 24.8 (CH_2^{Hex}), 22.6 (CH_2^{Hex}), 22.1 (CH_2^{Hex}), 20.8 (CH_3^{Tol}), 15.5 ($Me^{N=C}$) .

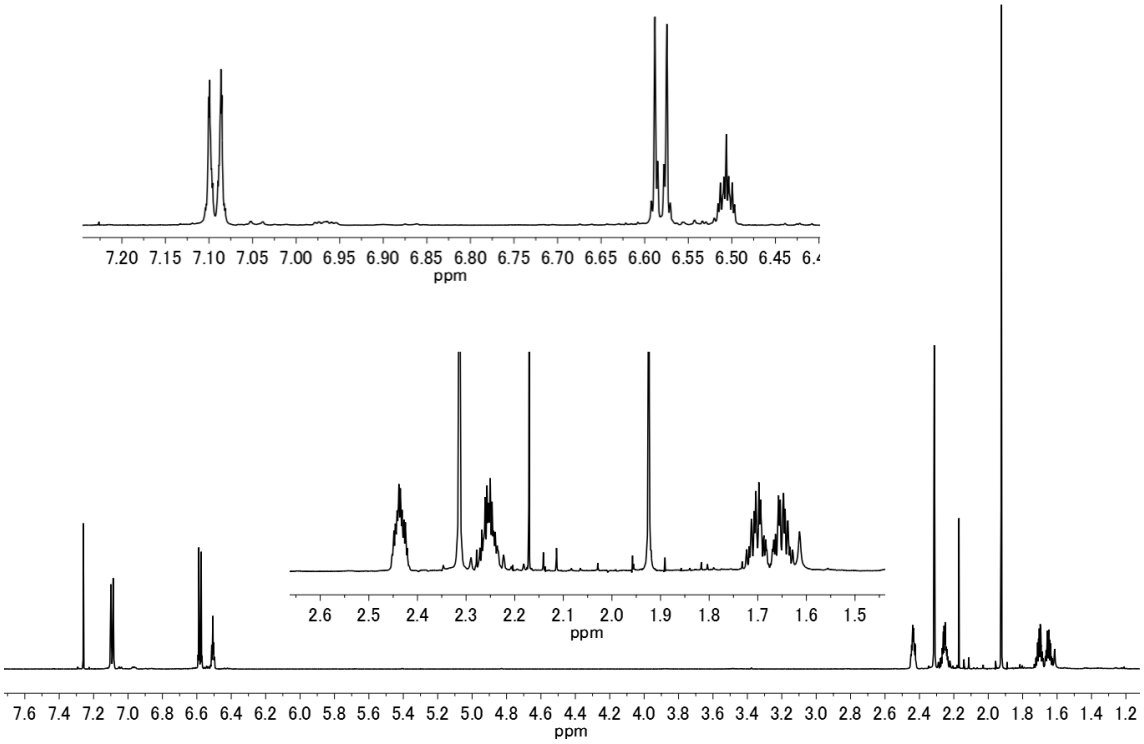


Figure S40 **^{1}H NMR** (600 MHz, $CDCl_3$, 299 K) spectrum of compound **12g**

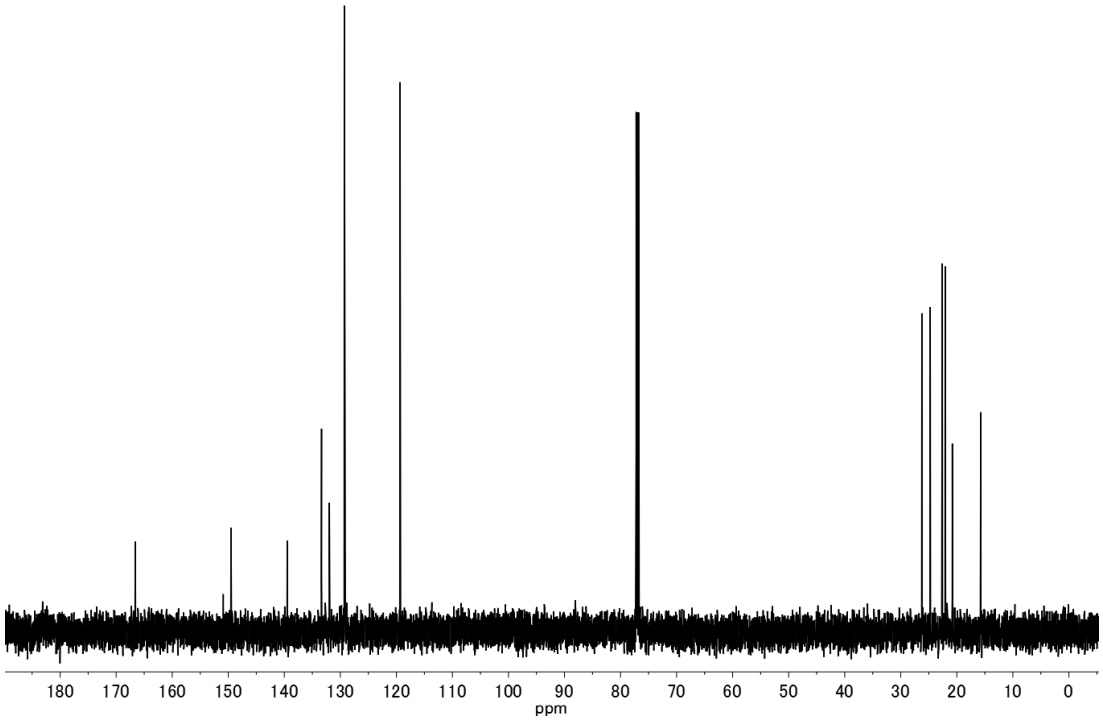
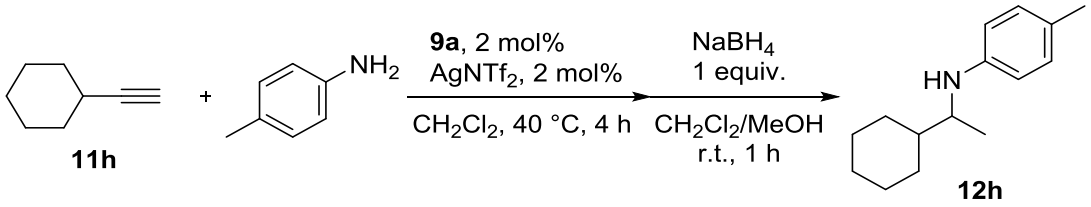


Figure S41 **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 299 K) spectrum of compound **12g**

Preparation of compound 12h:

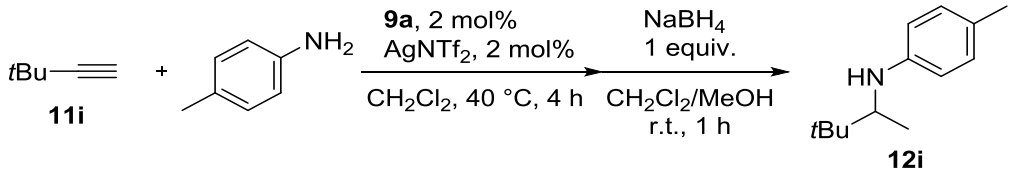


Scheme S17

A solution of cyclohexylacetylene (**11h**, 130 μL, ca. 1.0 mmol), toluidine (107 mg, 1.0 mmol), compound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. Then, MeOH (1 mL) and $NaBH_4$ were added to the mixture and stirred for 1 hour at room temperature. After quenching with H_2O (1 mL), the organic compounds were extracted by Et_2O (10 mL). The ethereal solution was dried over Na_2SO_4 and all volatiles were removed *in vacuo*. After the purification by silica gel column chromatography (pentane/acetone = 9/1), compound **12h** was obtained as a brown oil (120 mg, 0.55 mmol, 55% isolated). The NMR data were in good agreement with those given in the literature. [C. Brahms, P. Tholen, W. Saak, S. Doye, *Eur. J. Org. Chem.* **2013**, 7583–7592].

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 7.00 (m, 2H, CH^{Tol}), 6.53 (m, 2H, CH^{Tol}), 3.36 (br, 1H, NH), 3.32 (m, 1H, NCH), 2.27 (s, 3H, Me^{Tol}), 1.87-1.70 (m, 5H, CH_2^{Hex}), 1.48 (m, 1H, CH_2^{Hex}), 1.35-0.97 (m, 5H, CH_2^{Hex}) 1.14 (md, *J* = 6.3 Hz, 3H, CHCH_3).

Preparation of compound 12i:



Scheme S18

A solution of *tert*-butylacetylene (**11i**, 122 μL, ca. 1.0 mmol), toluidine (107 mg, 1.0 mmol), compound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. Then, MeOH (1 mL) and $NaBH_4$ were added to the mixture and stirred for 1 hour at room temperature. After quenching with H_2O (1 mL), organic compounds were extracted by Et_2O (10 mL). The ethereal solution was dried over Na_2SO_4 and all volatiles were removed *in vacuo*. After the purification by silica gel column chromatography (pentane/acetone = 9/1), compound **12i** was obtained as a brown oil (112 mg, 0.59 mmol, 59% isolated).

HRMS: m/z calc. for $C_{13}H_{21}N+[H^+]$ 192.1752; found 192.1756

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 6.98 (m, 2H, CH^{Tol}), 6.54 (m, 2H, CH^{Tol}), 3.26 (br, 1H, NH), 3.20 (q, $^3J_{HH}$ = 6.5 Hz, 1H, NCH), 2.24 (s, 3H, Me^{Tol}), 1.09 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CHCH_3), 0.97 (m, 9H, Me^{tBu}).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 299 K): δ = 146.3 (C^{Tol}), 129.7 (CH^{Tol}), 125.7 (C^{Tol}), 113.2 (CH^{Tol}), 57.6 (NCH), 34.7 (C^{tBu}), 26.5 (Me^{tBu}), 20.3 (Me^{Tol}), 15.8 (CHCH_3).

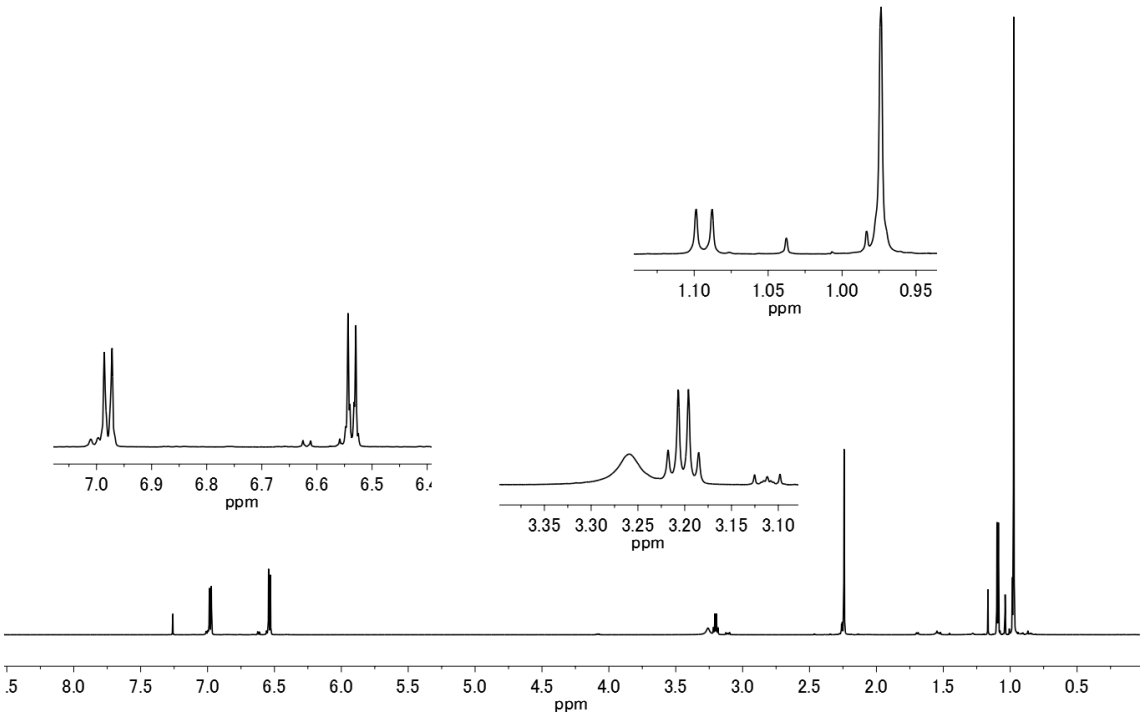


Figure S42 **^{1}H NMR** (600 MHz, $CDCl_3$, 299 K) spectrum of compound **12i**

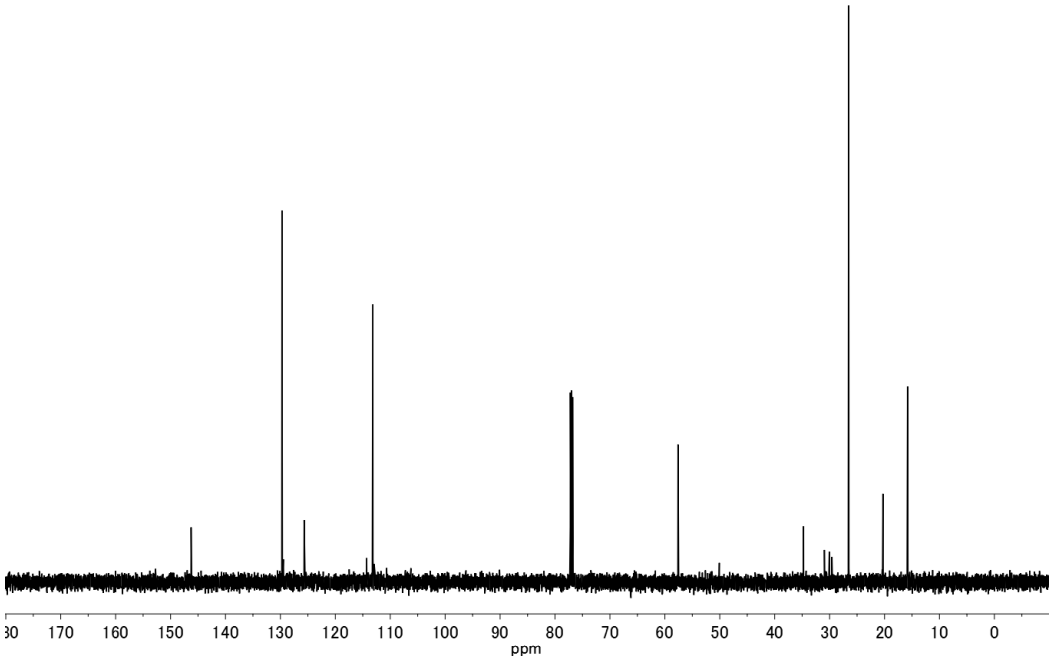
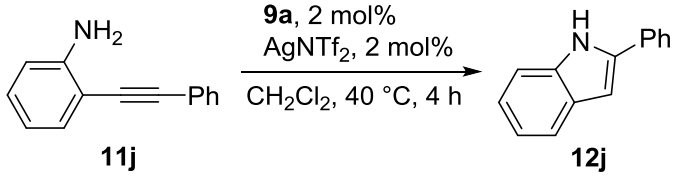


Figure S43 **^{13}C{^{1}H} NMR** (151 MHz, $CDCl_3$, 299 K) spectrum of compound **12i**

Preparation of compound 12j:



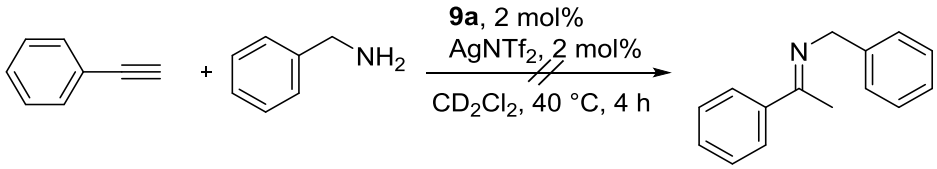
11j **12j**

Scheme S19

A solution of 2-(phenylethynyl)aniline (**11j**, 193 mg, 1.0 mmol), compound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CH_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. The suspension was filtered and the filtrate was concentrated *in vacuo.* After the purification by silica gel column chromatography (pentane/acetone = 9/1), compound **12j** was obtained as a white powder (180 mg, 0.93 mmol, 93% isolated). [P. R. Marqués, M. A. R. Crespo, A. L. Pérez, A. Corma *J. Am. Chem. Soc.*, **2015**, *137*, 11832].

^{1}H NMR (600 MHz, $CDCl_3$, 299 K): δ = 8.33 (br, 1H, NH), 7.67 (d, *J* = 7.8 Hz, 2H, Ph), 7.64 (d, *J* = 7.8 Hz, 1H, Ind), 7.45 (t, *J* = 7.3 Hz, 2H, Ph), 7.41 (d, *J* = 7.8 Hz, 1H, Ind), 7.33 (t, *J* = 7.3 Hz, 2H, Ph), 7.20 (t, *J* = 7.8 Hz, 2H, Ind), 7.13 (t, *J* = 7.8 Hz, 2H, Ind), 6.84 (s, 1H, 3-CH^{Ind}).

Reaction of benzyl amine as aliphatic amine:



Scheme S20

A solution of phenylacetylene (102 mg), benzylaniline (107 mg, 1.0 mmol), compound **9a** (19 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.8 mg, 0.02 mmol, 2 mol%) in CD_2Cl_2 (1 mL) was stirred for 4 hours at 40 °C. Then the reaction mixture was characterized by ^{1}H NMR experiments: no conversion to the hydroamination product was observed.

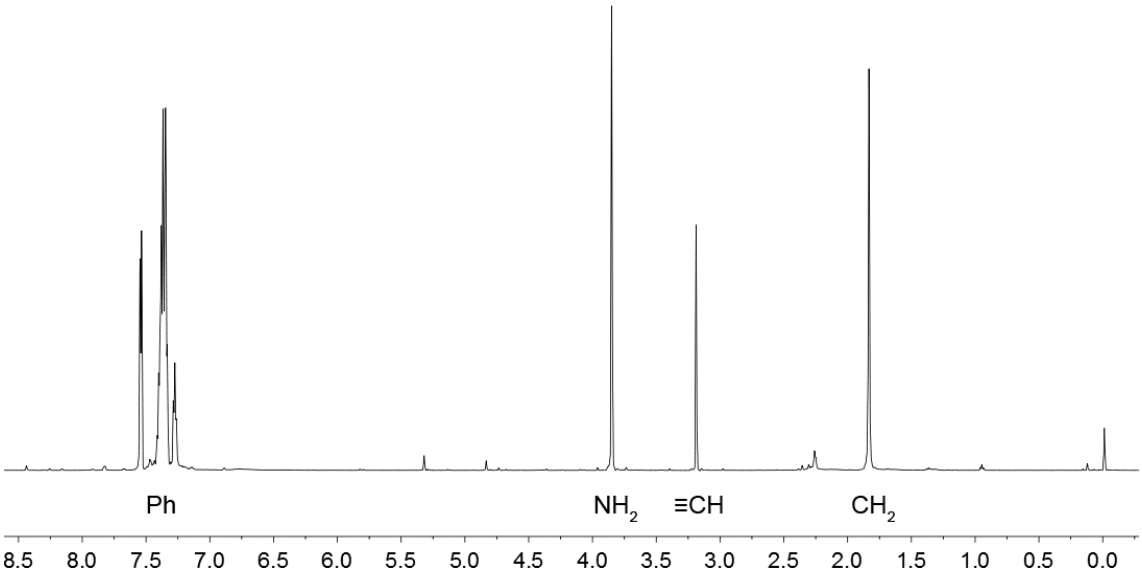
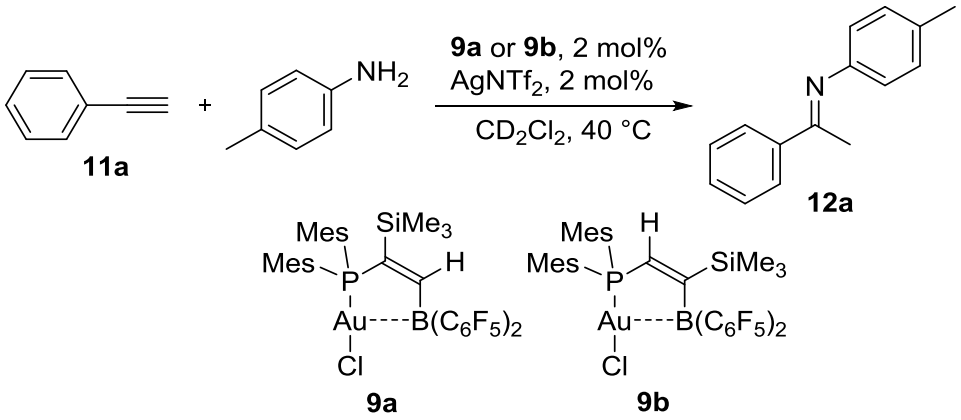


Figure S44 **^{1}H NMR** (600 MHz, CD_2Cl_2, 299 K) spectrum of the reaction mixture.

Catalytic hydroamination reaction: Time-conversion curve with compounds 9a or 9b.



Scheme S21

A solution of phenylacetylene (**11a**, 102 mg, 1.0 mmol), *p*-toluidine (107 mg, 1.0 mmol), compounds **9a**/**b** (18.8 mg, 0.02 mmol, 2 mol%), and $AgNTf_2$ (7.7 mg, 0.02 mmol, 2 mol%) in CD_2Cl_2 (2 mL) was sealed in a J-Young NMR tube and heated at 40 °C. Then, the % yields of the imine product were determined by ^1H NMR analysis after 0.5, 1, 2, and 4 h reaction time.

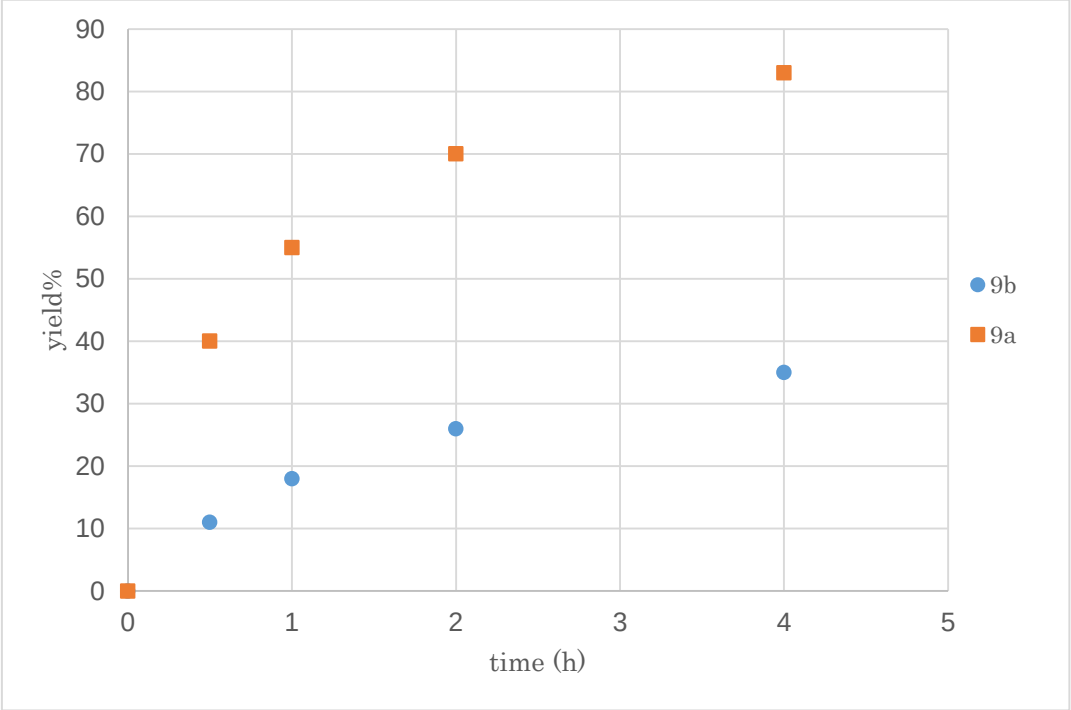
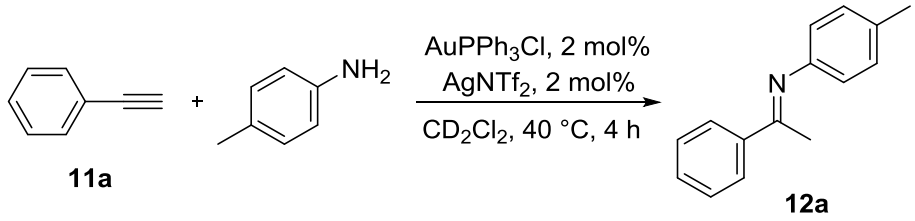


Figure S45 Time-conversion curves of the hydroamination reaction of phenylacetylene with *p*-toluidine with compounds **9a** and **9b**

Control reaction: hydroamination reaction in the presence of $AuPPh_3Cl$



Scheme S22

A solution of phenylacetylene (26 mg, 0.25 mmol), *p*-toluidine (27 mg, 0.25 mmol), $AuPPh_3Cl$ (2.5 mg; 0.005 mmol, 2 mol%), $AgNTf_2$ (1.9 mg; 0.005 mmol, 2 mol%) in CD_2Cl_2 (0.5 mL) was heated for 4 hours at 40 °C. Then the reaction mixture was characterized by ^1H NMR experiments: hydroamination product was observed in ca. 28 mol% yield.

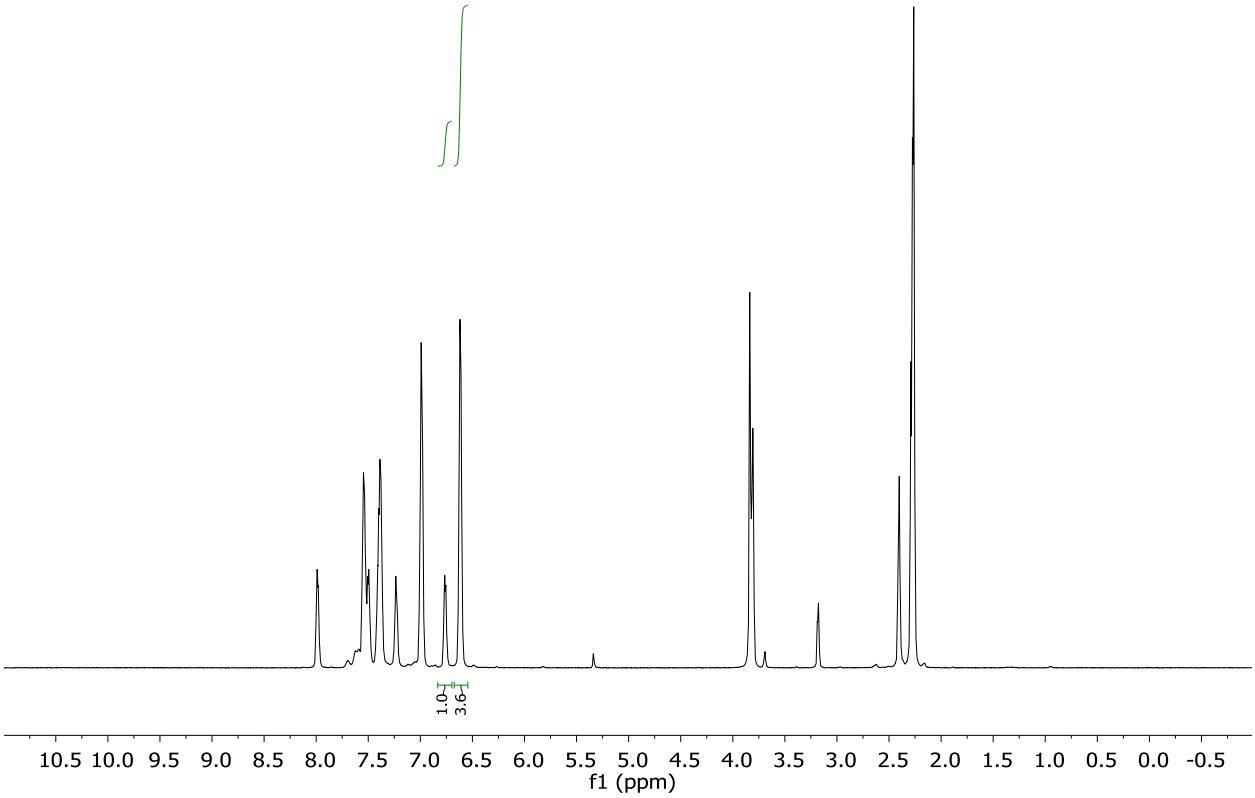


Figure S46 **^1H NMR** (600 MHz, CD_2Cl_2, 299 K) hydroamination reaction of phenylacetylene with *p*-toluidine in the presence of 2 mol% of $AuPPh_3Cl$ with 2 mol% of $AgNTf_2$.