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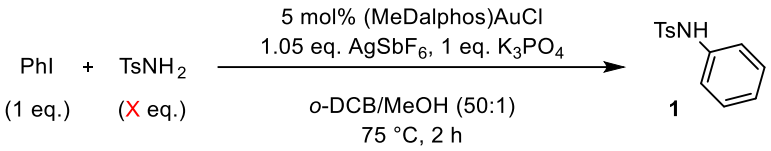
Materials and methods

Unless otherwise stated, all reactions and manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques or in a glovebox under an inert atmosphere. Dry, oxygen-free solvents were employed. Solution ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on Bruker Avance 300, 400 or 500 spectrometers at 298K unless otherwise stated. Chemical shifts (δ) are expressed with a positive sign, in parts per million. ^{1}H and ^{13}C chemical shifts are referenced internally to residual protio (^{1}H) or deutero (^{13}C) solvent, while ^{31}P, ^{19}F and ^{15}N chemical shifts are relative to 85% H_3PO_4, $CFCl_3$ and NH_3 respectively. The following abbreviations and their combinations are used: br, broad; s, singlet; d, ldoublet; t, triplet; q, quartet; m, multiplet. GC-MS analyses were performed on a MS Perkin Elmer Clarus MS560, GC PerkinElmer Clarus 500 and Agilent HP6890. All commercial starting materials were used as received unless otherwise stated. All starting materials were purchased from Aldrich and used as received unless otherwise stated.

Experimental procedures and analytical data

Optimization of the reaction conditions

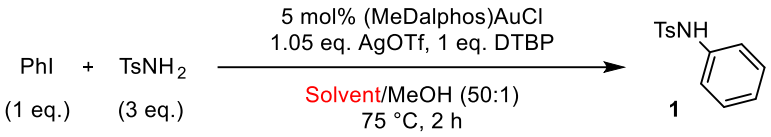
Ratio of the coupling partners



Entry	Eq.	Yield 2 h
1	1 eq.	10%
2	**3 eq.**	**79%**

Table S1. Influence of the coupling partner ratio. Cross-coupling of iodobenzene and *p*-toluenesulfonamide catalyzed by (MeDalphos)AuCl. Yields determined using calibrated GC-MS with *n*-dodecane as internal standard.

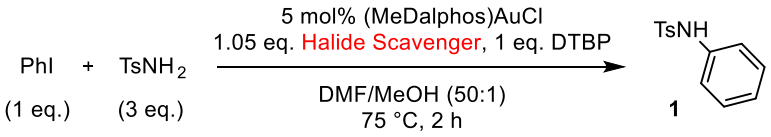
Screening of solvents



Entry	Solvent	Yield 2 h
1	***o*-DCB**	**99%**
2	DMF	92%
3	DMSO	91%
4	Nitromethane	98%
5	Acetonitrile	0%

Table S2. Screening of solvents. Cross-coupling of iodobenzene and *p*-toluenesulfonamide catalyzed by (MeDalphos)AuCl. Yields determined using calibrated GC-MS with *n*-dodecane as internal standard.

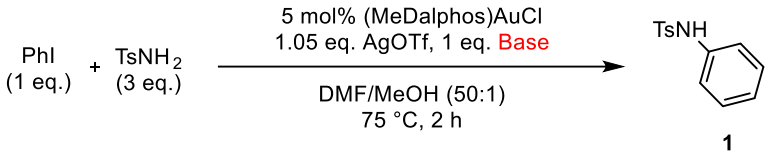
Screening of halide scavengers



Entry	Halide Scavenger	Yield 2 h
1	**AgOTf**	**99%**[a]
2	None	0%
3	$AgNTf_2$	74%[a]
4	$Cu(OTf)_2$	0%
5	$Cu(MeCN)_4BF_4$	7%
6	$NaBAr^F$	0%
7	KPF_6	0%

Table S3. Screening of halide scavengers. Cross-coupling of iodobenzene and *p*-toluenesulfonamide catalyzed by (MeDalphos)AuCl. Yields determined using calibrated GC-MS with *n*-dodecane as internal standard. [a]Reaction run in DCB/MeOH (50:1).

Screening of bases

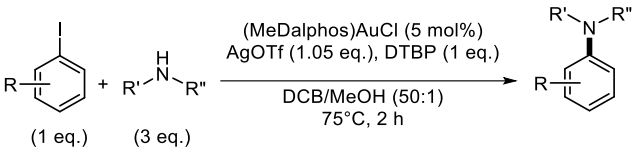


1

Entry	Halide Scavenger	Yield 2 h
1	**DTBP**	**99%** [a]
2	K^{t}OBu	0%
3	Cs_2CO_3	0%
4	Proton Sponge®	13%
5	Lutidine	0%
6	DIEA	3%

Table S4. Screening of the bases. Cross-coupling of iodobenzene and *p*-toluenesulfonamide catalyzed by (MeDalphos)AuCl. Yields determined using calibrated GC-MS with *n*-dodecane as internal standard. [a]Reaction run in DCB/MeOH (50:1).

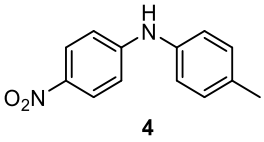
General procedure for gold-catalyzed arylation of *N*-nucleophiles with aryl iodides



In a glovebox, a flame dried Schlenk equipped with a magnetic stirrer bar was charged with silver triflate (49 mg, 0.19 mmol, 1.05 eq.), DTBP (41 µL, 0.18 mmol, 1 eq.) and the *N*-nucleophile (0.54 mmol, 3 eq.) and dissolved in *o*-dichlorobenzene (0.9 mL*). (MeDalphos)AuCl (6 mg, 9 µmol) was transferred into a small glass vial and dissolved in *o*-dichlorobenzene (0.9 mL*). The aryl iodide (0.18 mmol, 1 eq.), and methanol (36 µL) were added to the gold complex solution. This solution was loaded into a plastic syringe equipped with stainless steel needle. The syringe was closed by blocking the needle with a septum. Outside the glovebox, the Schlenk was cooled down to -10°C (Ethanol/N_2 cold bath). At this temperature, the solution of (MeDalphos)AuCl and the aryl iodide was added. The reaction mixture was then stirred at 75°C. Yields were determined using NMR vs. *n*-dodecane as internal standard.

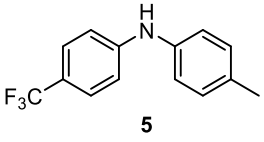
After complete conversion, silver salts were filtrated, and the solvent evaporated. Isolated yields were determined after column chromatography. The fractions containing the coupling product were then concentrated under vacuum to yield the pure product.

Analytical data of the coupling products **1** and **2** were compared and identical to those of commercial samples.



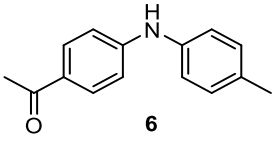
4

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.40-7.00 (m, $H_{aromatic}$), 6.50 (br s, 1H, NH), 2.36 (s, 3H, CH_3). **MS** (m/z): calcd for $C_{13}H_{12}N_2O_2$: 228.09, found: 228.00. Analytical data are consistent with those previously reported in the literature.[1]



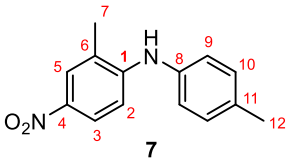
5

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-6.80 (m, $H_{aromatic}$), 2.34 (s, 3H, CH_3).**MS** (m/z): calcd for $C_{14}H_{12}F_3N$: 251.09, found: 250.88. Analytical data are consistent with those previously reported in the literature.[2]



6

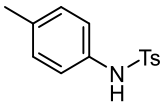
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-6.60 (m, $H_{aromatic}$), 6.05 (br s, 1H, NH), 2.53 (s, 3H, CH_3 acetyl), 2.35 (s, 3H, CH_3 tolyl). **MS** (m/z) calcd for $C_{15}H_{15}NO$: 225.12, found: 225.03. Analytical data are consistent with those previously reported in the literature.[2]



7

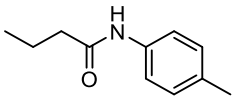
Crude purified by column chromatography (20% ethyl acetate in pentane), to afford an orange solid (166 mg, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 2.7 Hz, 1H, H_5), 7.95 (dd, *J* = 2.7 Hz, 9.08 Hz, 1H, H_3), 7.21 (d, *J* = 8.9 Hz, 2H, H_{10}), 7.11 (d, *J* = 8.9 Hz, 2H, H_9), 6.96 (d, *J* = 9.1 Hz, 1H, H_2), 5.88 (s, 1H, NH), 2.37 (s, 3H, H_{12}), 2.33 (s, 3H, H_7). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 149.6 (C_4), 139.2 (C_1), 137.1 (C_8), 135.1 (C_{11}), 130.5 (C_{10}), 126.8 (C_5), 124.1 (C_3), 123.5 (C_9), 122.7 (C_6), 111.2 (C_2), 21.1 (C_{12}), 17.7 (C_7). **MS** (m/z): calcd for $C_{14}H_{14}N_2O_2$: 242.11, found 242.01.

* 0.45 mL for the scope of amines.



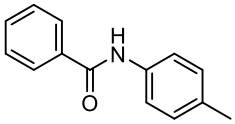
8

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-6.90 (m, $H_{aromatic}$), 2.36 (s, 3H, CH_3 tosyl), 2.27 (s, 3H, CH_3 tolyl). **MS** (m/z): calcd for $C_{14}H_{15}NO_2S$: 261.08, found: 260.95. Analytical data are consistent with those previously reported in the literature.[3]



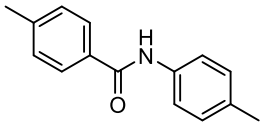
9

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.10 (m, $H_{aromatic}$), 2.4-2.3 (m, 5H, CH_2&CH_3 tolyl), 1.80 (sext, *J* = 7.5 Hz, 2H, CH_2), 1.04 (t, *J* = 7.5 Hz, 3H, CH_3). **MS** (m/z): calcd for $C_{11}H_{15}NO$: 177.12, found: 177.01. Analytical data are consistent with those previously reported in the literature.[4]



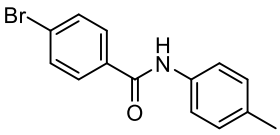
10

Crude purified by column chromatography (20% ethyl acetate in pentane), to afford a white solid (360 mg, 85%). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.93 – 7.75 (m, 3H), 7.64 – 7.43 (m, 5H), 7.18 (d, *J* = 8.2 Hz, 2H), 2.34 (s, 3H, CH_3). **MS** (m/z): calcd for $C_{14}H_{13}NO$ 211.10, found: 211.05. Analytical data are consistent with those previously reported in the literature.[5]



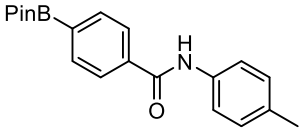
11

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-7.10 (m, $H_{aromatic}$), 2.42 (s, 3H, CH_3 tolyl), 2.34 (s, 3H, CH_3 tolyl). **MS** (m/z): 225.29 calcd for $C_{14}H_{13}NO$, found: 225.00 Analytical data are consistent with those previously reported in the literature.[5]



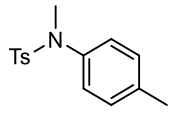
12

^{1}H NMR (300 MHz, MeOD): δ 8.00-6.80 (m, $H_{aromatic}$), 2.29 (s, 3H, CH_3 tolyl). **MS** (m/z): 289.01 calcd for $C_{14}H_{12}BrNO$, found: 291.00. Analytical data are consistent with those previously reported in the literature.[6]



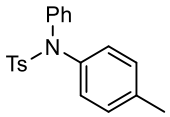
13

Crude purified by column chromatography (30% ethyl acetate in pentane), to afford an yellowish solid (110 mg, 45%). Crystals suitable for X-ray diffraction analysis were obtained by layering a DCM solution with pentane. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.96 – 7.90 (m, 2H), 7.90 – 7.85 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.15 (m, 2H), 2.36 (s, 3H), 1.39 (s, 12H). **^{13}C{^{1}H} NMR** (500 MHz, $CDCl_3$): δ 165.5 (Cq), 137.2 (Cq), 135.3 (Cq), 135.1 (CH), 134.3 (Cq), 129.6 (CH), 126.1 (CH), 120.3 (CH), 84.2 (Cq), 24.9 (CH_3), 20.9 (CH_3). **MS** (m/z): 337.18 calcd for: $C_{20}H_{24}BNO_3$, found: 337.10.



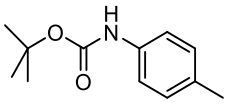
14

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-6.90 (m, $H_{aromatic}$), 3.15 (s, 3H, CH_3), 2.41 (s, CH_3 tosyl) 2.33 (s, 3H, CH_3 tolyl). **MS** (m/z): calcd for $C_{15}H_{17}NO_2S$: 275.10, found: 274.96. Analytical data are consistent with those previously reported in the literature.[7]



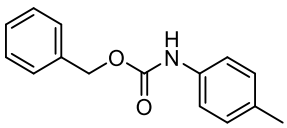
15

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70-6.90 (m, $H_{aromatic}$), 2.43 (s, 3H, CH_3 tosyl), 2.32 (s, 3H, CH_3 tolyl). **MS** (m/z): calcd for $C_{20}H_{19}NO_2S$: 337.11, found: 336.98. Analytical data are consistent with those previously reported in the literature.[8]



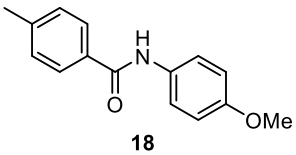
16

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.05 (m, $H_{aromatic}$), 2.30 (s, 3H, CH_3 tolyl), 1.53 (s, 9H, CH_3 *t*Bu). **MS** (m/z): calcd for $C_{12}H_{17}NO_2$: 207.13, found: 207.00. Analytical data are consistent with those previously reported in the literature.[9]



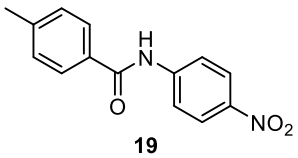
17

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.00 (m, $H_{aromatic}$), 5.20 (s, 2H, CH_2 benzyl), 2.30 (s, 3H, CH_3 tolyl). **MS** (m/z): calcd for $C_{15}H_{15}NO_2$: 241.11, found: 241.01. Analytical data are consistent with those previously reported in the literature.[10]



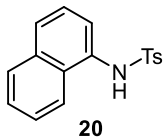
18

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79-6.92 (m, $H_{aromatic}$), 3.81 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3 tolyl). **MS** (m/z): 241.11 calcd for $C_{15}H_{15}NO_2$, found: 241.01. Analytical data are consistent with those previously reported in the literature.[11]



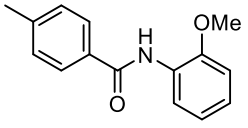
19

^{1}H NMR (300 MHz, C_6D_6): δ 9.44 (s, NH), 8.32-6.67 (m, $H_{aromatic}$), 2.40 (s, 3H, CH_3 tolyl). **MS** (m/z): 256.08 calcd for $C_{14}H_{12}N_2O_3$, found: 256.42. Analytical data are consistent with those previously reported in the literature.[11]



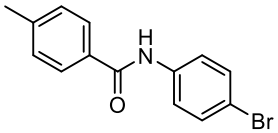
20

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90-6.80 (m, $H_{aromatic}$), 2.34 (s, 3H, CH_3 tosyl) **MS** (m/z): calcd for $C_{17}H_{15}NO_2S$ 297.08, found: 296.96. Analytical data are consistent with those previously reported in the literature.[12]



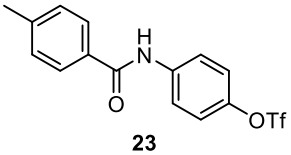
21

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.63-6.88 (m, $H_{aromatic}$), 3.93 (s, 3H, OCH_3), 2.43 (s, 3H, CH_3 tolyl). **MS** (m/z): 241.11 calcd for $C_{15}H_{15}NO_2$, found: 241.11. Analytical data are consistent with those previously reported in the literature.[13]



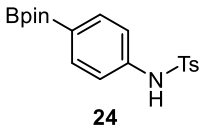
22

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80-7.16 (m, $H_{aromatic}$), 2.42 (s, 3H, CH_3 tolyl). **MS** (m/z): 289.01 calcd for $C_{14}H_{12}BrNO$, found: 288.96. Analytical data are consistent with those previously reported in the literature.[14]



23

Crude purified by column chromatography (80% dichloromethane in pentane), to afford a white solid (182 mg, 71%). Crystals suitable for X-ray diffraction analysis were obtained by layering a DCM solution with pentane. **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.90 (s, 1H), 7.69 (m, 4H), 7.22 (dd, *J* = 8.6 Hz, 4H), 2.35 (s, 3H, CH_3 tolyl). **^{13}C{^{1}H} NMR** (500 MHz, CD_2Cl_2): δ 165.5 (Cq), 145.3 (Cq), 143.0 (Cq), 138.5 (Cq), 131.5 (CH), 129.5 (CH), 127.0 (CH), 121.9 (CH), 118.8 (Cq, d, *J* = 320.7 Hz), 117.5, 29.7 (Cq), 21.2 (CH_3). **^{19}F NMR** (300 MHz, CD_2Cl_2): δ -75.36. **MS** (m/z): 359.04 calcd for $C_{15}H_{12}F_3NO_4S$, found: 358.98.



24

^{1}**H NMR** (300 MHz, $CDCl_3$): δ 7.90-6.90 (m, $H_{aromatic}$), 2.35 (s, 3H, CH_3 tosyl), 1.32 (s, 12H, CH_3 pinacol). Analytical data are consistent with those previously reported in the literature.[15]

NMR spectra for the coupling products (new compounds)

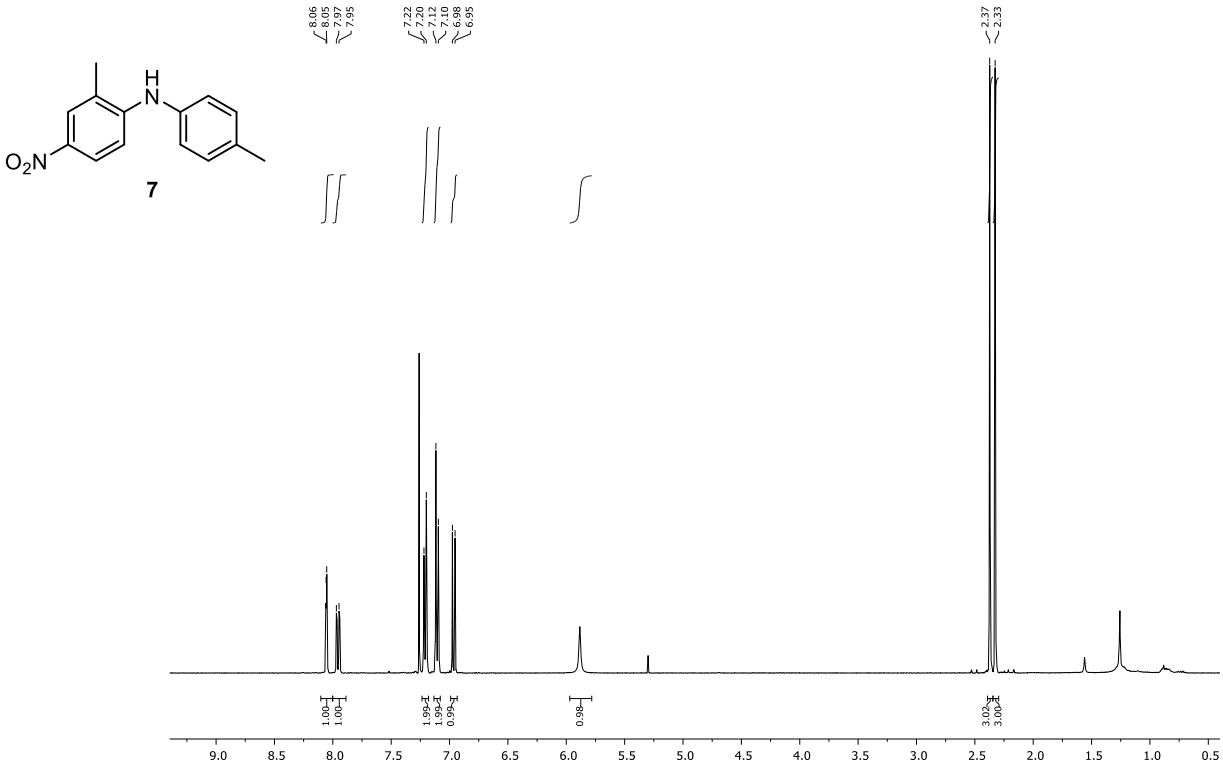


Figure S1. ^{1}H NMR spectrum of **7** in $CDCl_3$.

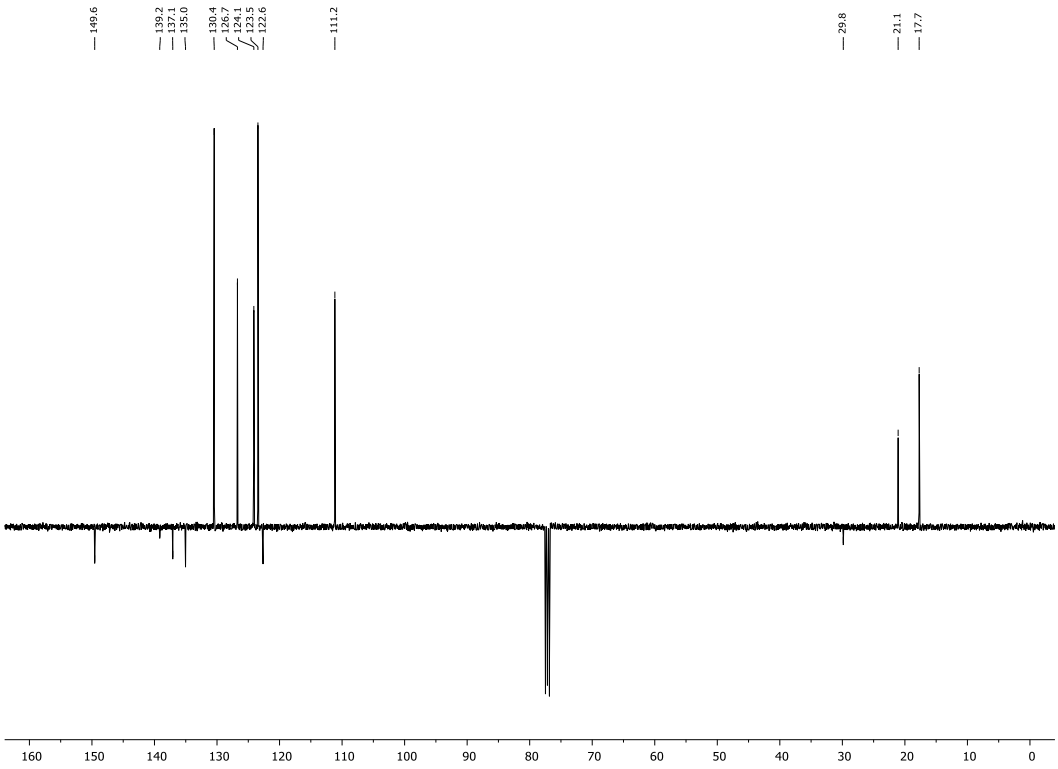


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.

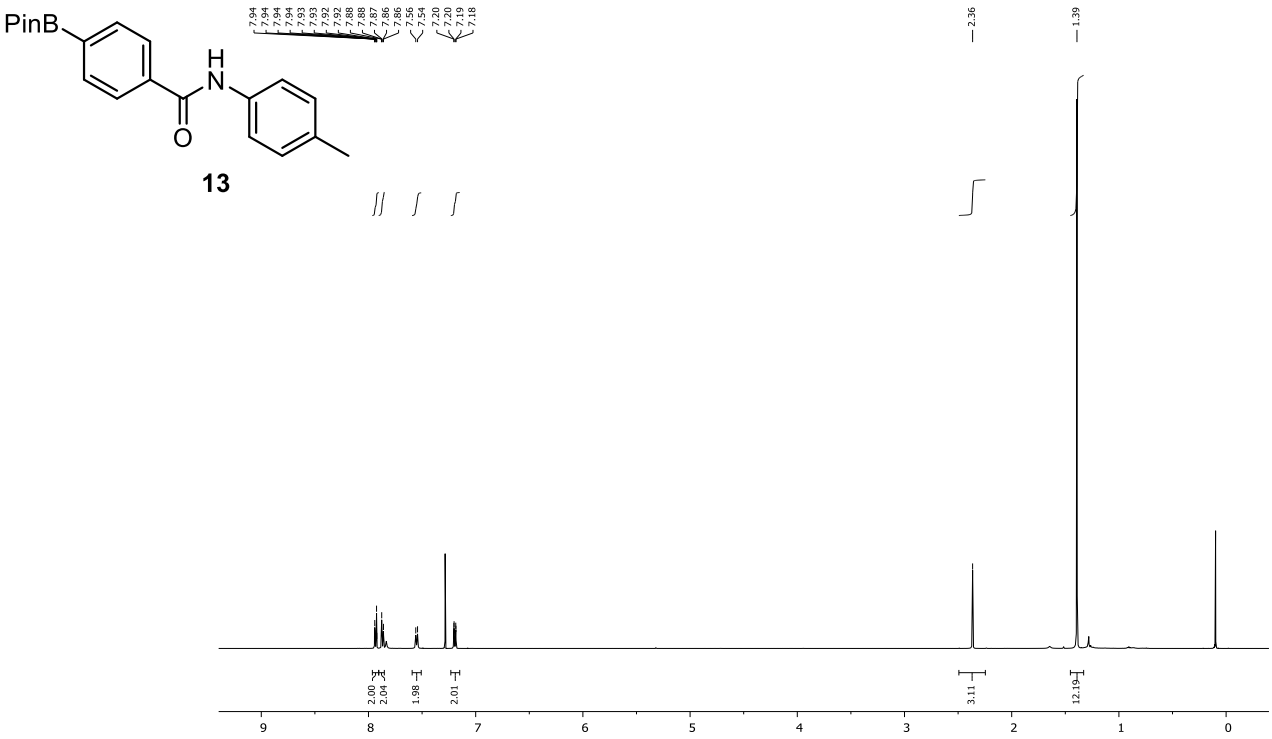


Figure S3. ^{1}H NMR spectrum of **13** in $CDCl_3$.

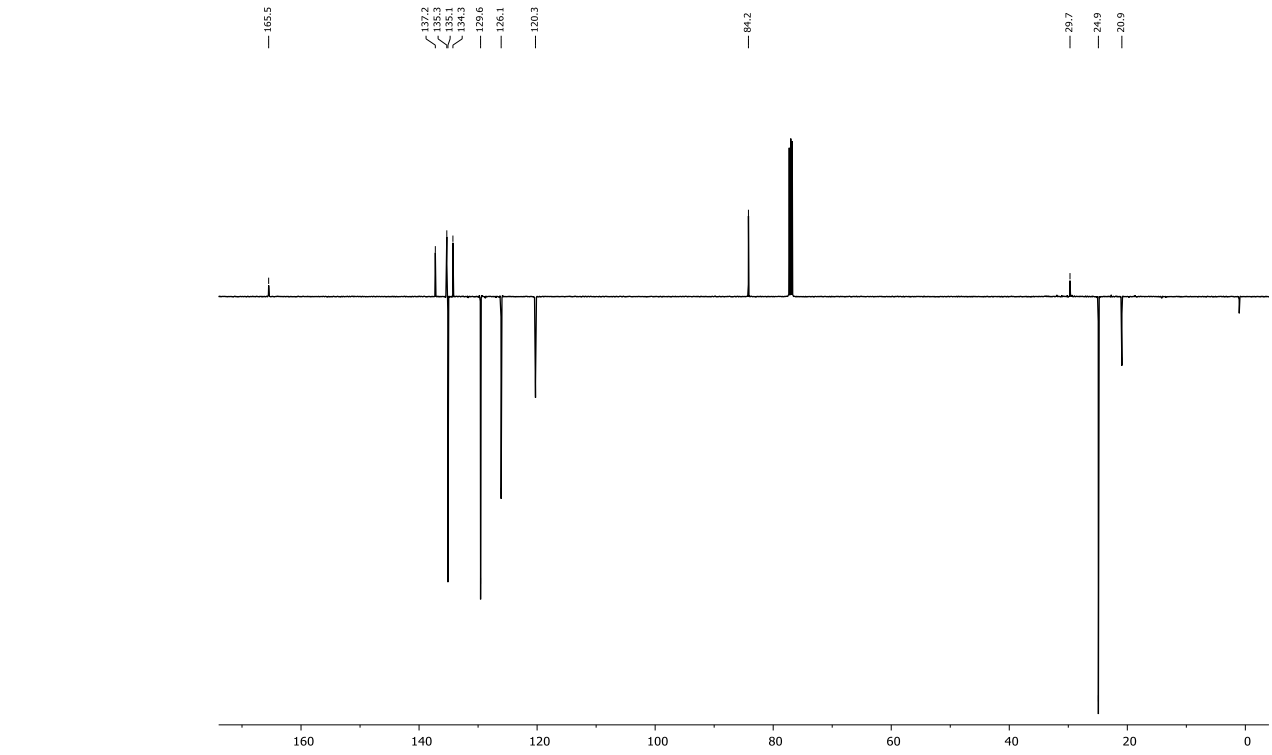


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **13** in CD_2Cl_2.

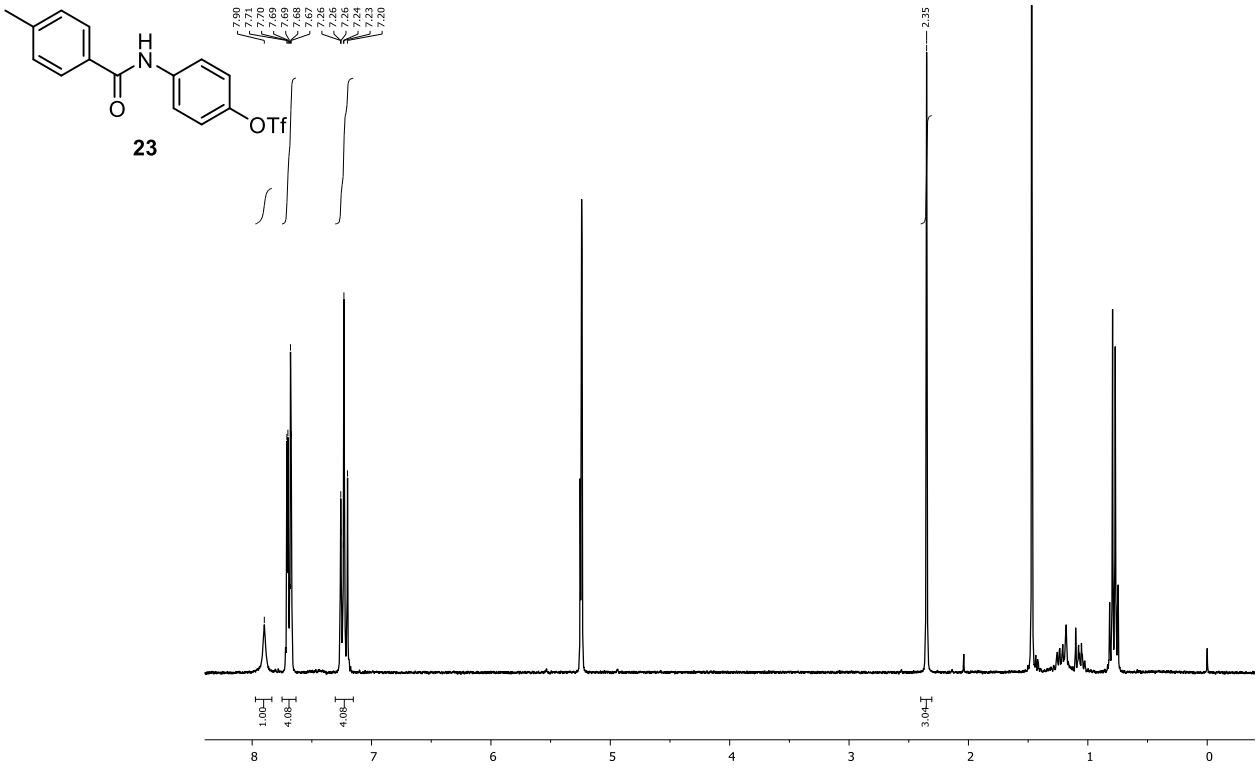


Figure S5. ^{1}H NMR spectrum of **23** in $CDCl_3$.

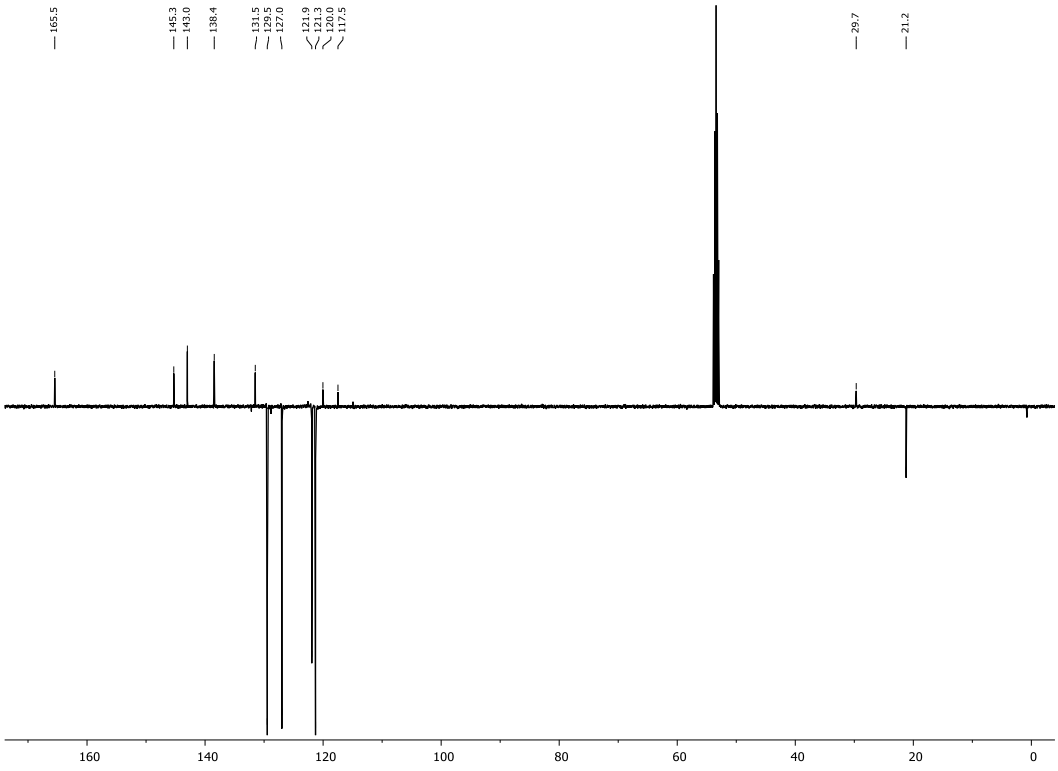


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **23** in CD_2Cl_2.

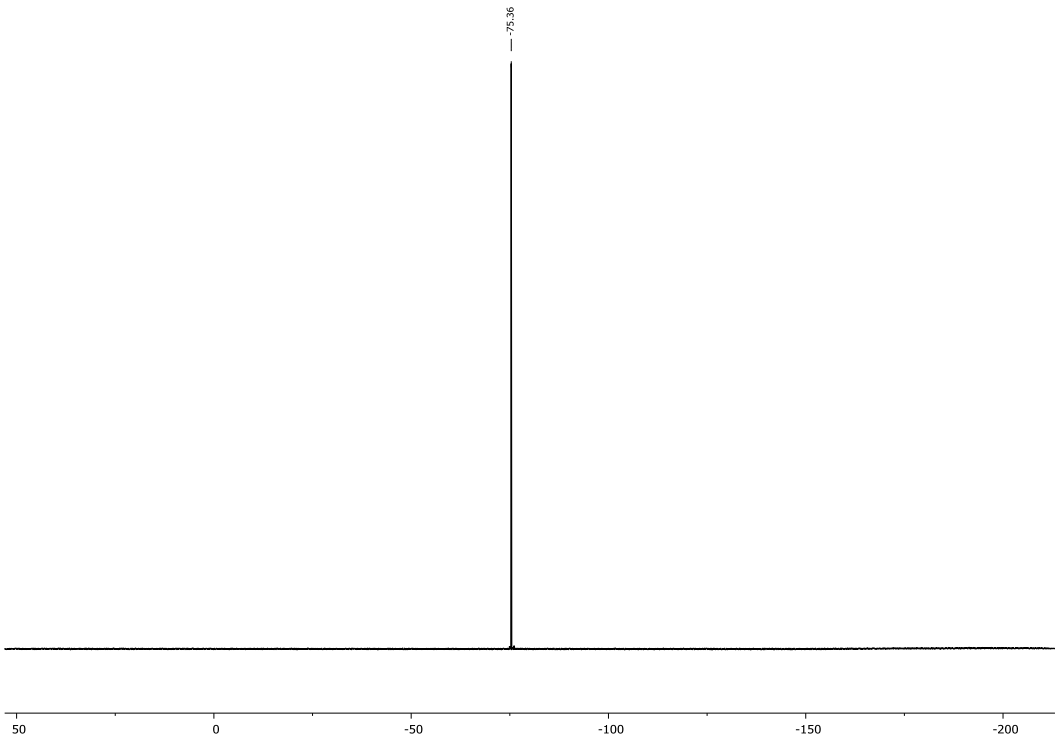
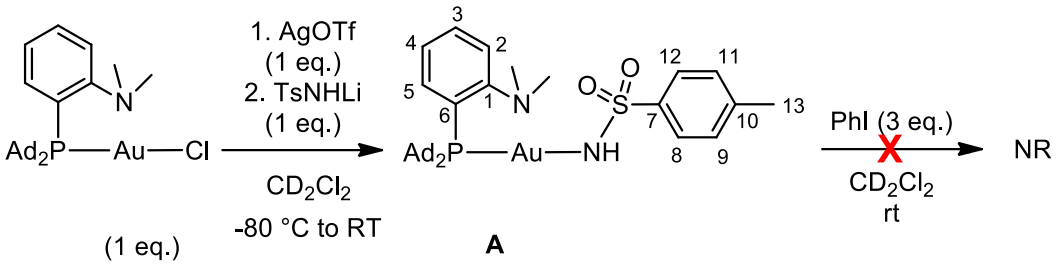


Figure S7. $^{19}F\{^{1}H\}$ NMR spectrum of **23** in CD_2Cl_2.

Synthesis of the Au(I)-amido complex A and test of oxidative addition



Preparation of TsNHLi: an oven dried Schlenk equipped with a magnetic stirring bar was charged with *p*-toluenesulfonamide (100 mg, 0.58 mmol) and dissolved in THF (1 mL). The Schlenk was cooled down to -78 °C (Ethanol/N_2 cold bath), and *n*-BuLi (0.36 mL of a 1.6 M solution, 0.58 mmol, 1 eq.) was added dropwise and the reaction mixture left stirring for 30 min and then brought back to room temperature. A white suspension was obtained and used as such for further reactions.

Synthesis of Au(I)-amido complex A: A screw-cap NMR tube was charged with (MeDalphos)AuCl complex (26 mg, 0.04 mmol) and silver triflate (10 mg, 0.04 mmol) and dissolved in CD_2Cl_2 (0.6mL) and the suspension of TsNHLi (100 µL of a 0.4 M suspension, 0.04 mmol, 1 eq.) was added at rt. The tube was gently shaken and the progress of the reaction was followed by ^{31}P and ^{1}H NMR, observing an instantaneous reaction. The solution was filtered over celite. Evaporation of the solvent afforded a white solid. Crystals of **A**.2LiOTf suitable for X-ray diffraction analysis were obtained by layering a DCM solution with pentane. Lithium triflate was removed by redissolving the crude in DCM and filtering over basic alumina (^{19}F NMR using 1 eq. of α,α,α-trifluorotoluene as internal standard shows the quantitative removal of the triflate).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.96 (d, J_{HH} = 8.3 Hz, 2H, H_8 & H_{12}), 7.76 (ddd, J_{HH} = 8.1 Hz, J_{HP} = 6.7 Hz, J_{HH} = 1.6 Hz, 1H, H_2), 7.59 (m, 1H, H_4), 7.54 (m, 1H, H_3), 7.33 (m, 1H, H_5), 7.20 (d, J_{HH} = 8.0 Hz, 2H, H_9 & H_{11}), 4.22 (s, 1H, NH), 2.57 (s, 6H, N(CH_3)$_2$), 2.38 (s, 3H, H_{13}), 2.26 – 1.93 (m, 18H, H_{Ad}), 1.77 – 1.56 (m, 12H, H_{Ad}).

^{31}P NMR (300 MHz, CD_2Cl_2): δ 54.27.

^{13}C{^{1}H} NMR (500 MHz, CD_2Cl_2): δ 160.8 (d, J_{PC} = 7.3 Hz, C_6), 144.4 (s, C_7), 140.7 (s, C_{10}), 135.0 (s, C_2), 132.5 (s, C_4), 128.8 (s, C_9 & C_{11}), 126.0 (s, C_8 & C_{12}), 125.8 (d, J_{PC} = 4.5 Hz, C_3), 124.6 (d, J_{PC} = 6.7 Hz, C_5), 122.2 (d, J_{PC} = 48.6 Hz, C_1), 46.7 (s, N($\underline{C}H_3$)$_2$), 42.0 (s, CH_{2Ad}), 41.3 (d, J_{PC} = 24.3 Hz, C_{qAd}), 36.3 (s, CH_{2Ad}), 28.7 (d, J_{PC} = 9.8 Hz, CH_{Ad}), 21.1 (s, C_{13}).

^{15}N NMR (500 MHz, CD_2Cl_2): δ 110.2 (d, J_{PN} = 37 Hz, $\underline{N}$HTs), 38.1 (s, $\underline{N}(CH_3)_2$).

(MeDalphos)AuCl: **^{15}N NMR** (500 MHz, CD_2Cl_2): δ 37.0.

Oxidative addition test: In a glovebox, a screw-cap NMR tube was charged with complex **A** (10 mg, 0.013 mmol) and CD_2Cl_2 (0.5 mL). Iodobenzene (4.2 µL, 0.039 mmol, 3 eq.) was added to the solution of the gold complex. The tube was gently shaken and the monitored by ^{31}P and ^{1}H NMR, observing no reaction.

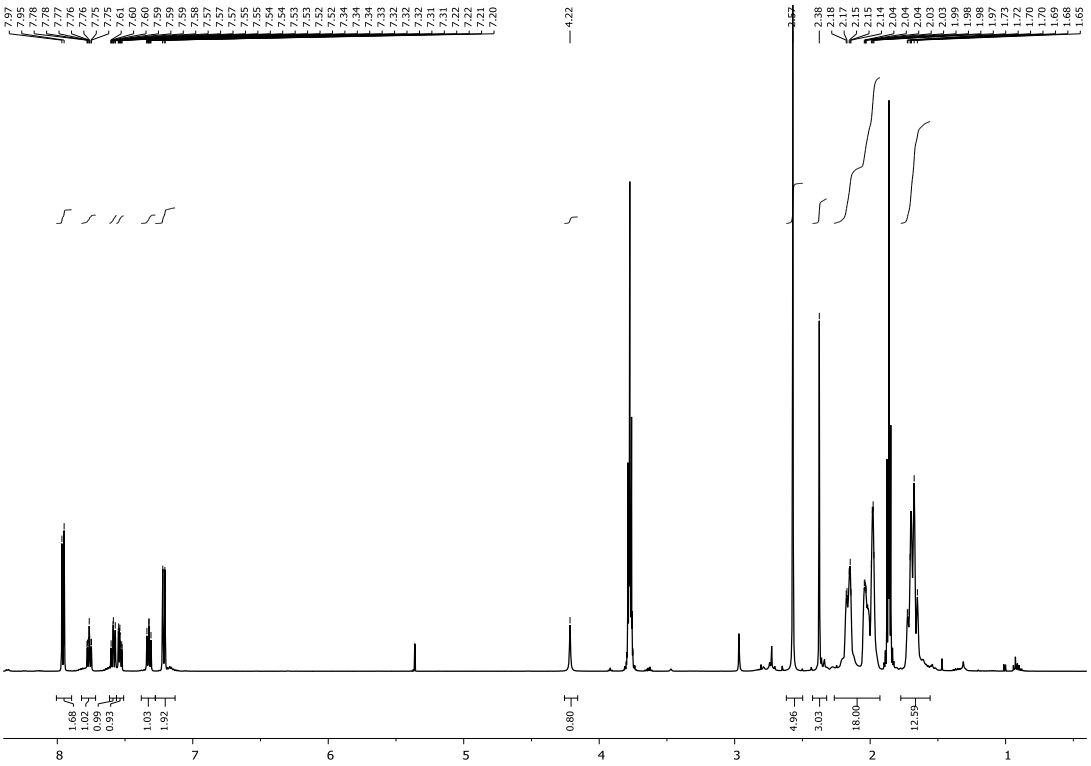


Figure S8. ^{1}H NMR spectrum of **A** in CD_2Cl_2.

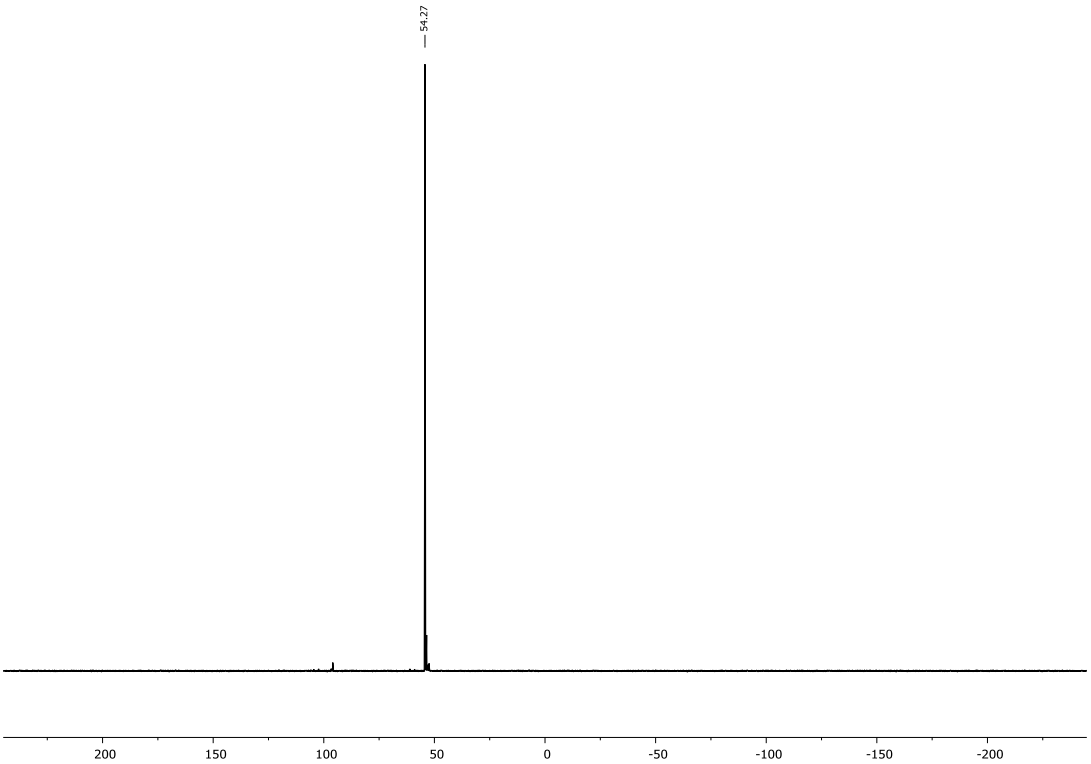


Figure S9. ^{31}P NMR spectrum of **A** in CD_2Cl_2.

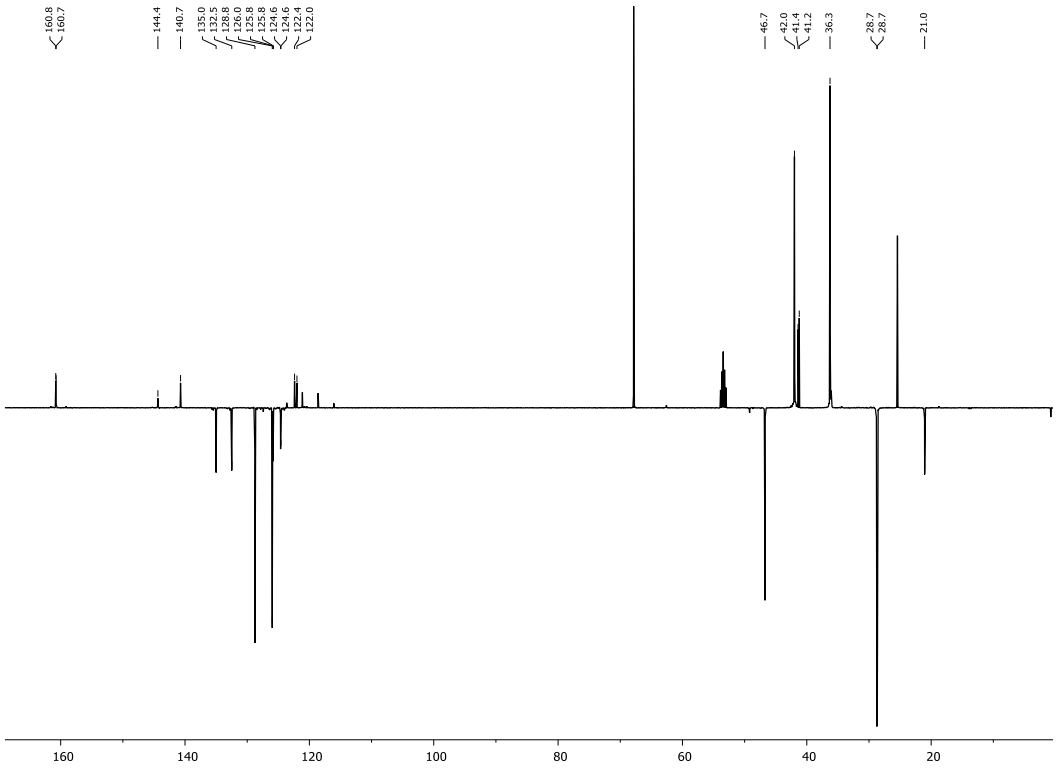


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **A** in CD_2Cl_2.

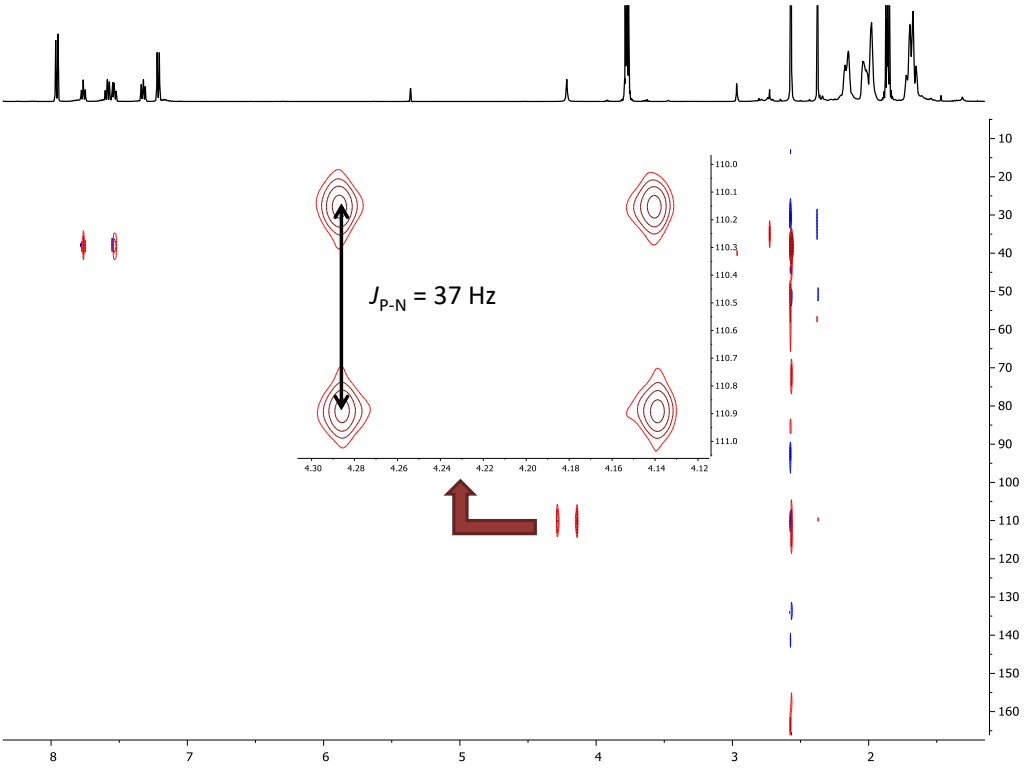


Figure S11. HSQC ^{1}H-^{15}N NMR spectrum of **A** in CD_2Cl_2.

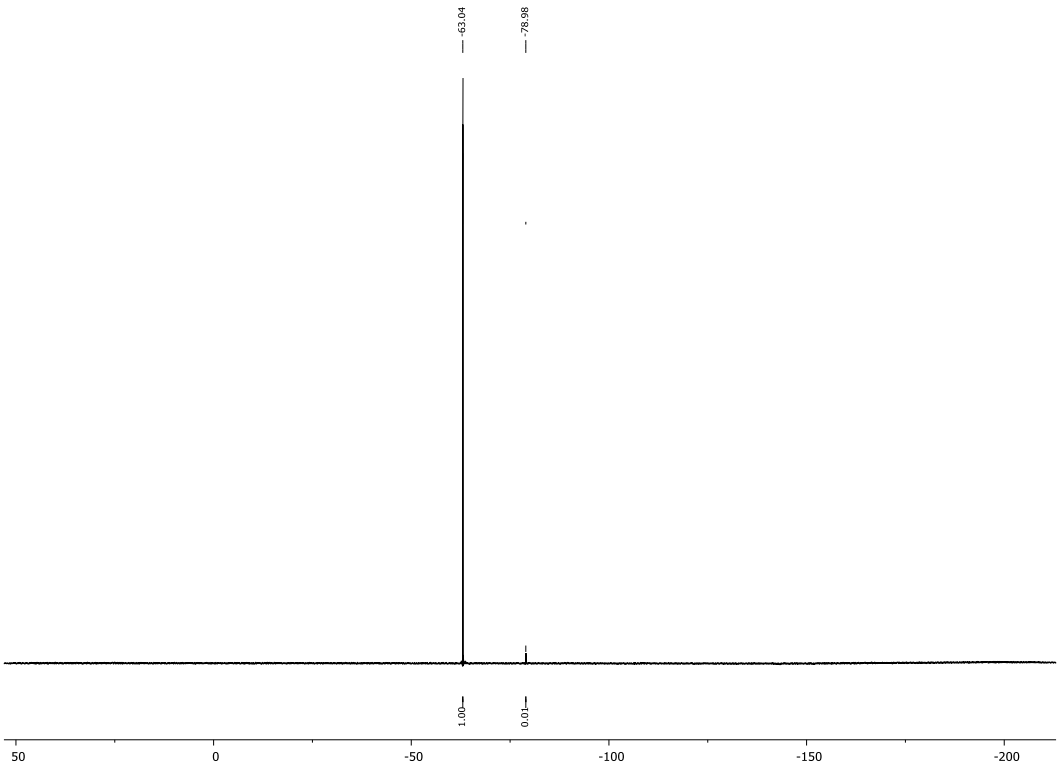


Figure S12. ^{19}F NMR spectrum of **A** in CD_2Cl_2 using 1 eq. of α,α,α-trifluorotoluene as internal standard.

General procedure for the oxidative addition of iodobenzene to the (P,N) gold(I) complex

In a glovebox, a screw-cap NMR tube was charged with silver hexafluoroantimonate (8.0 mg, 0.023 mmol), the corresponding amine when present (0.023 mmol) and CD_2Cl_2 (0.3 mL). (MeDalphos)AuCl complex (15 mg, 0.023 mmol) was transferred into a small glass vial and dissolved in CD_2Cl_2 (0.3 mL). Iodobenzene (2.6 µL, 0.023 mmol) was added to the solution of the gold complex. The prepared solution was loaded into a plastic syringe equipped with stainless steel needle. The syringe was closed by blocking the needle with a septum. Outside the glovebox, the NMR tube was cooled down to -80°C (Ethanol/N_2 cold bath). At this temperature, the solution of gold complex and iodobenzene was added. The tube was gently shaken and allowed to warm to rt. The formation of the gold(III) complex was confirmed by ^{1}H and ^{31}P NMR spectroscopy.[16]

B: **^{15}N NMR** (500 MHz, CD_2Cl_2): δ 71.5.

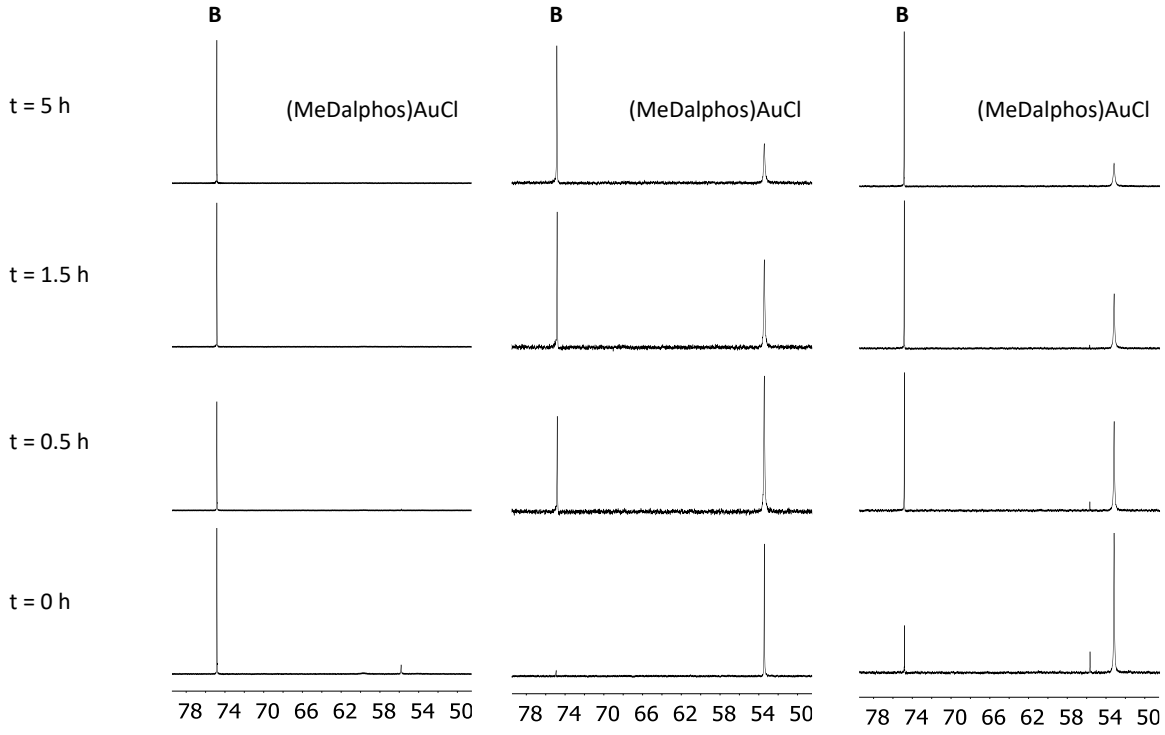
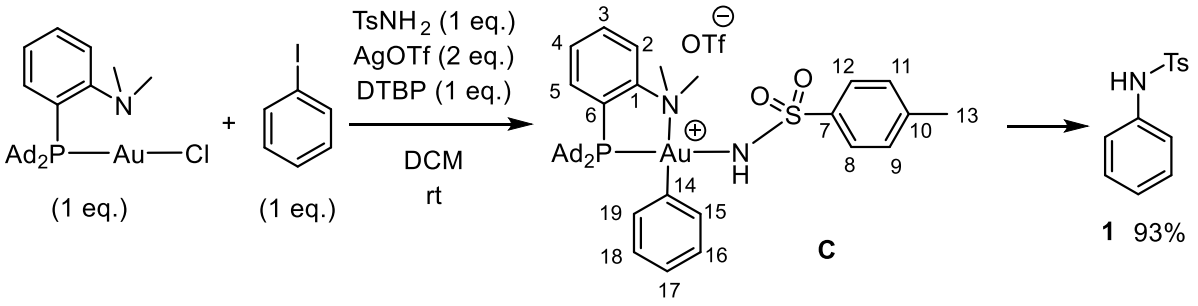


Figure S13. Evolution with time of the ^{31}P NMR spectrum for the oxidative addition of iodobenzene in the presence of *p*-nitroaniline (left), aniline (center) and *p*-anisidine (right).

Procedure for the stoichiometric reaction from Au(I) at rt



In a glovebox, a screw-cap NMR tube was charged with silver triflate (12 mg, 0.046 mmol, 2 eq.), *p*-toluenesulfonamide (4 mg, 0.023 mmol, 1 eq.), di-*tert*-butylpyridine (5.2 µL, 0.023 mmol, 1 eq.), and CD_2Cl_2 (0.3 mL). In a glass vial, (MeDalphos)AuCl complex (15 mg, 0.023 mmol) and iodobenzene (2.6 µL, 0.023 mmol, 1 eq.) were dissolved in CD_2Cl_2 (0.3 mL). The solution was loaded into a plastic syringe equipped with a stainless-steel needle. The syringe was closed by blocking the needle with a septum. Outside the glovebox, the NMR tube was cooled down to -80 °C (Ethanol/N_2 cold bath). At this temperature, the solution of gold complex and iodobenzene was added. The tube was gently shaken and allowed to warm to rt. The reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. Yield of **1** was determined by ^{1}H NMR with *n*-dodecane as internal standard.

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.99 (ddd, J_{HP} = 8.6 Hz, J_{HH} = 3.9 Hz, J_{HH} = 1.2 Hz, 1H, H_5), 7.93 (ddt, J_{HH} = 8.5 Hz, J_{HP} = 7.0 Hz, J_{HH} = 1.5 Hz, 1H, H_4), 7.89 (ddd, J_{HH} = 8.2 Hz, J_{HP} = 6.9 Hz, J_{HH} = 1.4 Hz, 1H, H_2), 7.84 (dd, J_{HH} = 8.2 Hz, J_{HH} = 1.9 Hz, 1H, H_{17}), 7.69 (m, 3H, H_3 & H_{15} & H_{19}), 7.38 (m, 2H, H_8 & H_{12}), 7.07 (m, 4H, H_9 & H_{11} & H_{16} & H_{18}), 5.10 (s, 1H, NH), 3.43 (s, 6H, N(CH_3)$_2$), 2.37 (s, 3H, H_{13}), 2.30 (m, 6H, H_{Ad}), 2.05 (m, 12H, H_{Ad}), 1.76 (m, 12H, H_{Ad}).

^{31}P NMR (300 MHz, CD_2Cl_2): δ 62.75.

^{13}C{^{1}H} NMR (500 MHz, CD_2Cl_2): δ 159.1 (d, J_{PC} = 7.5 Hz, C_6), 143.1 (s, C_7), 141.0 (s, C_{10}), 136.2 (s, C_2), 135.8 (s, C_4), 135.1 (s, C_{15} & C_{19}), 129.2 (s, C_3), 128.9 (s, C_9 & C_{11}), 127.9 (s, C_{14}), 127.2 (s, C_{16} & C_{18}), 125.2 (d, J_{PC} = 7.2 Hz, C_5), 124.9 (s, C_8 & C_{12}), 122.0 (s, C_{17}), 119.9 (d, J_{PC} = 44.0 Hz, C_1), 52.8 (s, N(CH_3)$_2$), 46.3 (d, J_{PC} = 15.7 Hz, C_{qAd}), 40.0 (s, CH_{2Ad}), 35.5 (d, J_{PC} = 1.9 Hz, CH_{2Ad}), 28.5 (d, J_{PC} = 9.8 Hz, CH_{Ad}), 21.0 (s, C_{13}).

^{15}N NMR (500 MHz, CD_2Cl_2): δ 117.8 (d, J_{PN} = 36.0 Hz, NHTs), 72.8 (s, N(CH_3)$_2$).

PhNHTs (coupling product): **^{15}N NMR** (500 MHz, CD_2Cl_2): δ 122.4.

HRMS (ESI$^+$): calcd. for $[M]^+$ = $C_{41}H_{53}AuN_2O_2PS$: 865.3231. Found: 865.3232.

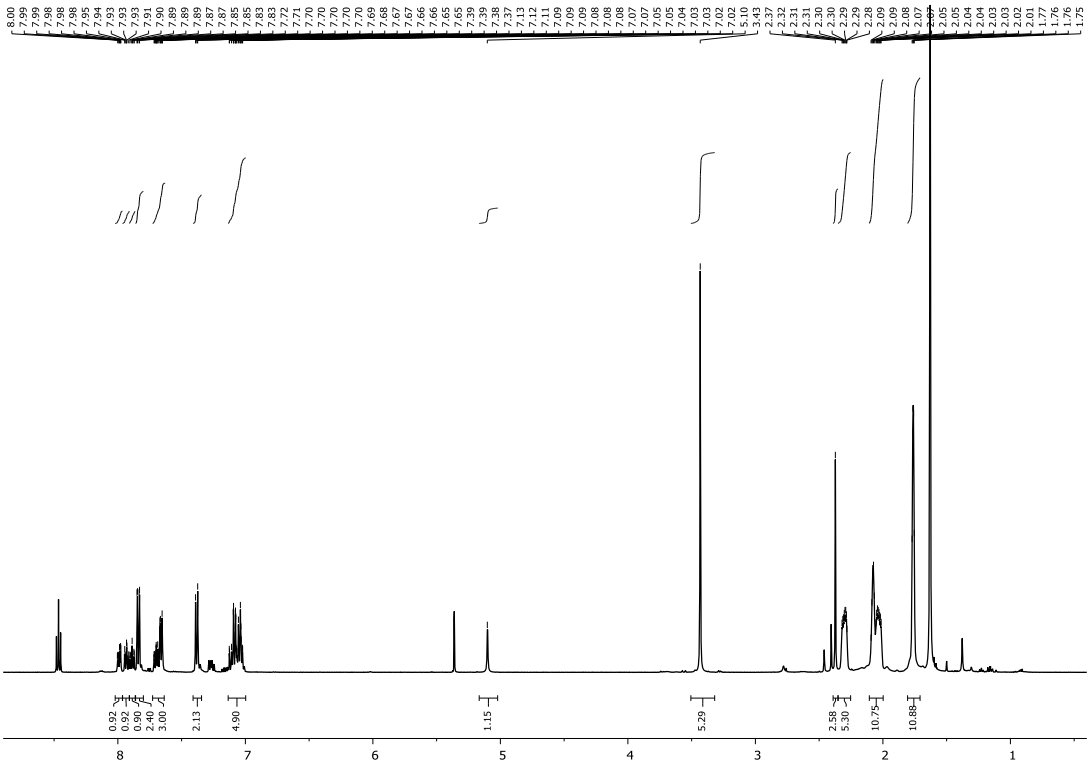


Figure S14. ^{1}H NMR spectrum of **C** in CD_2Cl_2.

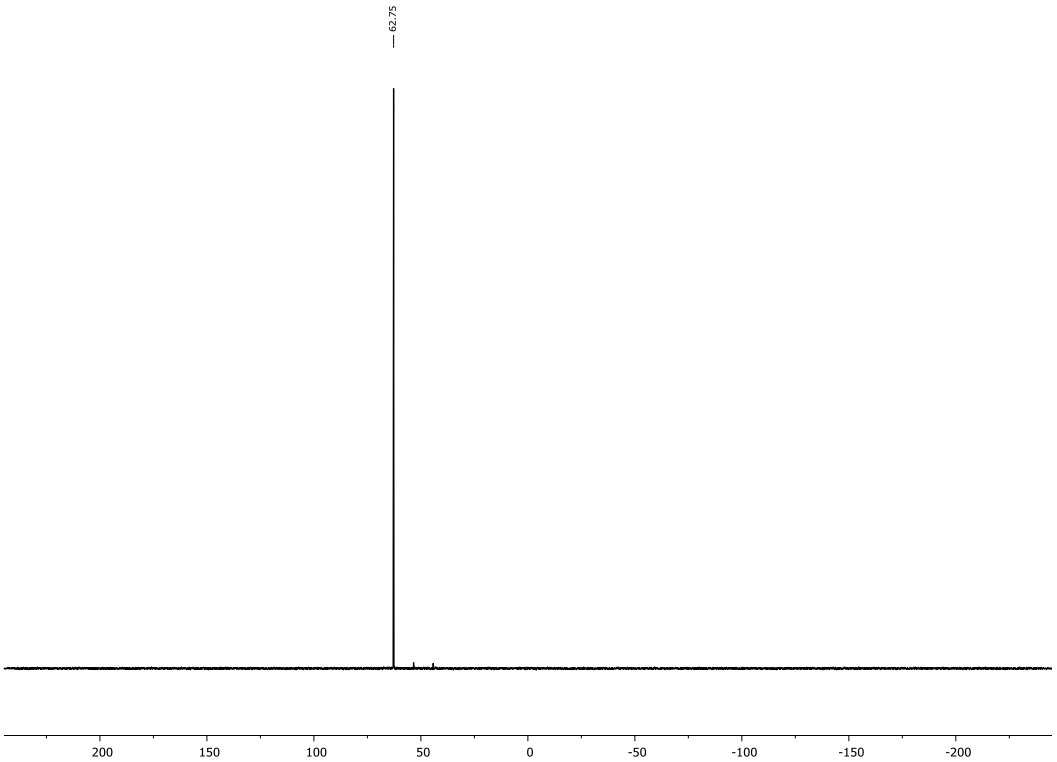


Figure S15. ^{31}P NMR spectrum of **C** in CD_2Cl_2.

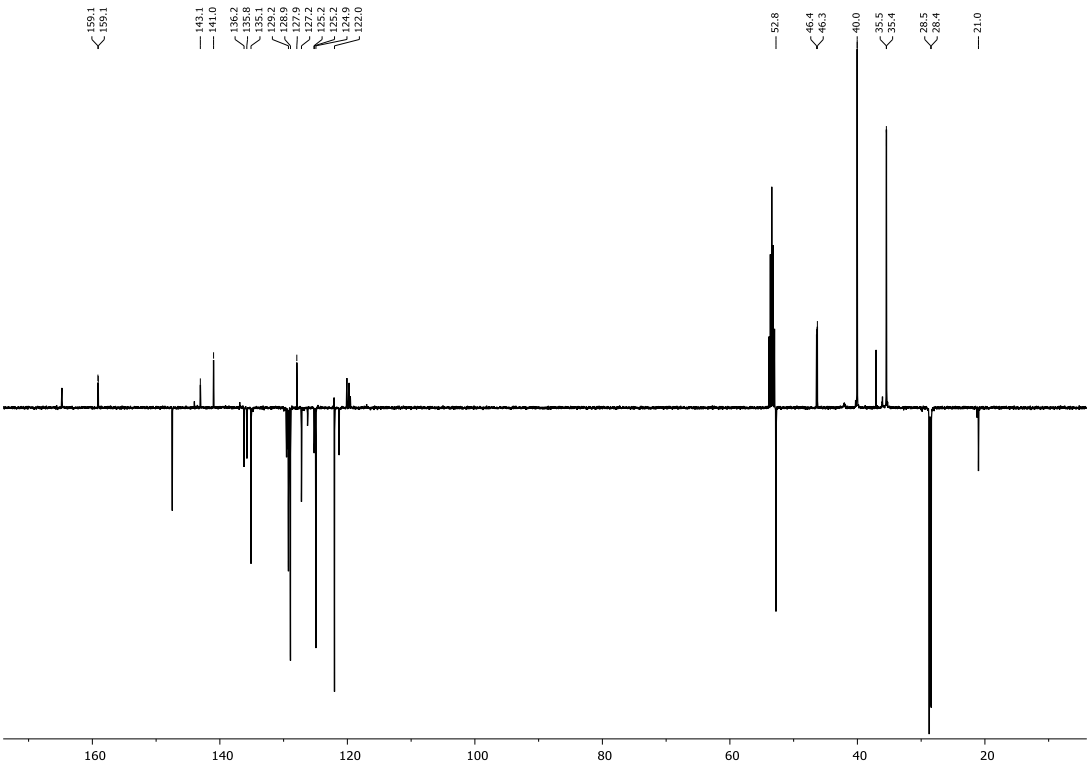


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **C** in CD_2Cl_2.

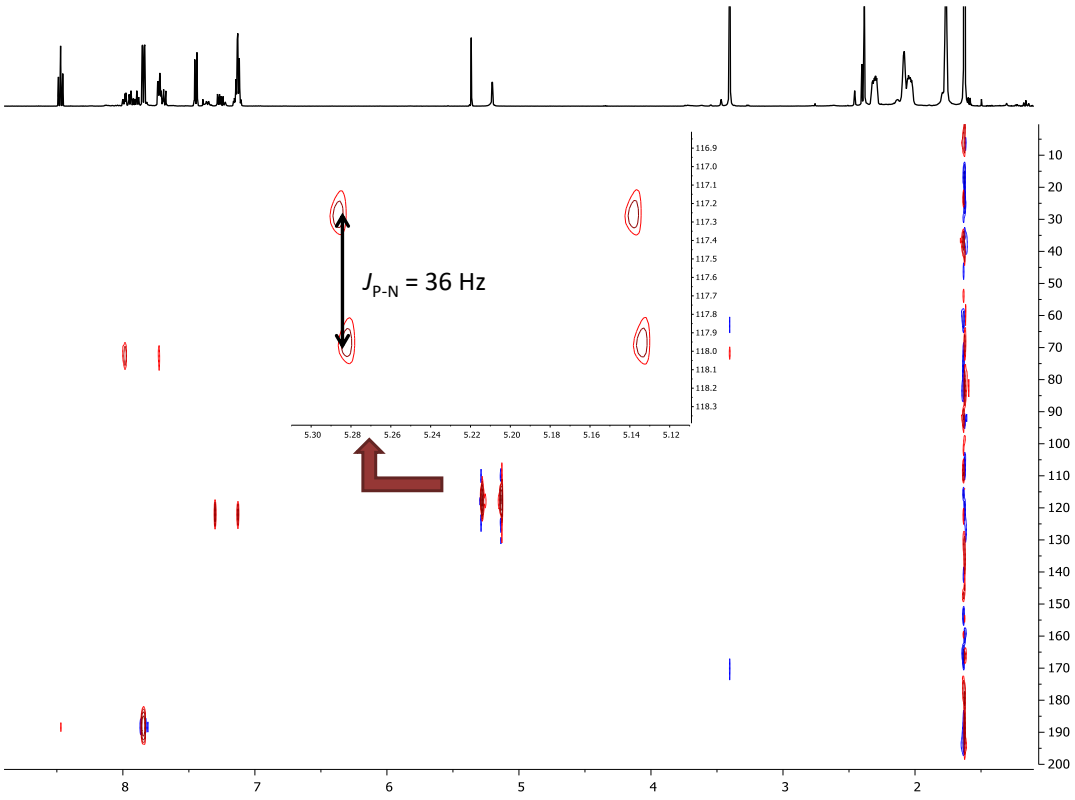
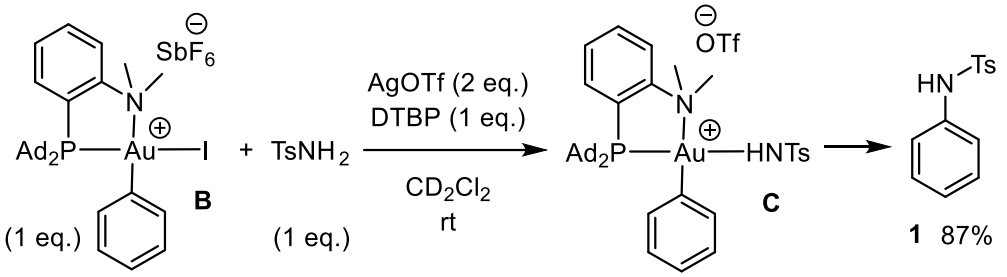


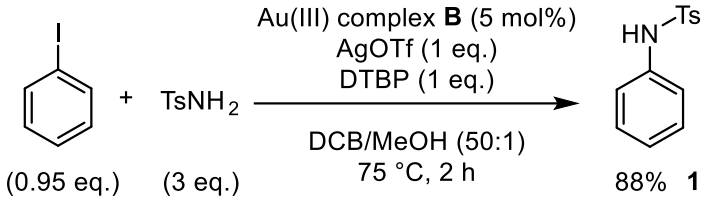
Figure S17. HSQC ^{1}H-^{15}N NMR spectrum of **C** in CD_2Cl_2.

Procedure for the stoichiometric reaction from the Au(III) complex B at rt



In a glovebox, a screw-cap NMR tube was charged with silver triflate (12 mg, 0.046 mmol, 2 eq.), *p*-toluenesulfonamide (4 mg, 0.023 mmol, 1 eq.), di-*tert*-butylpyridine (5.2 µL, 0.023 mmol, 1 eq.), and CD_2Cl_2 (0.3 mL). In a glass vial, Au(III) complex **B** (24 mg, 0.023 mmol) was dissolved in CD_2Cl_2 (0.3 mL). The solution was loaded into a plastic syringe equipped with a stainless-steel needle. The syringe was closed by blocking the needle with a septum. Outside the glovebox, the NMR tube was cooled down to -80 °C (Ethanol/N_2 cold bath). At this temperature, the solution of gold complex was added. The tube was gently shaken and allowed to warm to rt. The reaction was monitored by ^1H and ^{31}P NMR spectroscopy. Yield of **1** was determined by ^1H NMR with *n*-dodecane as internal standard.

Procedure for the catalytic reaction starting from the Au(III) complex B



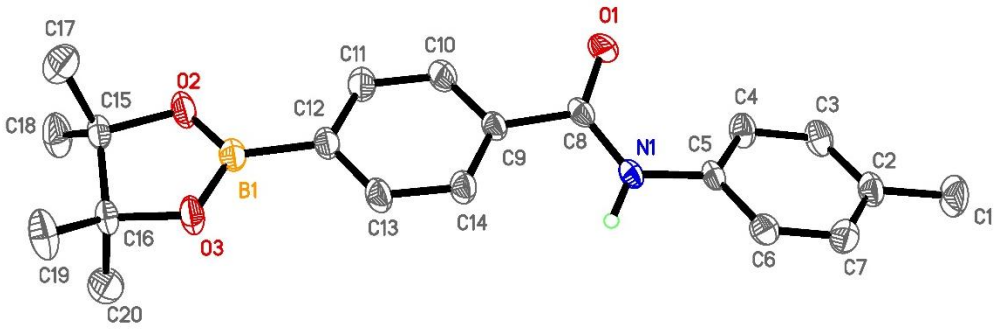
In a glovebox, a flame dried Schlenk equipped with a magnetic stirrer bar was charged with the *p*-toluenesulfonamide (93 mg, 0.54 mmol, 3 eq.), silver triflate (49 mg, 0.18 mmol, 1 eq.) DTBP (41 µL, 0.18 mmol, 1 eq.) and *o*-dichlorobenzene (0.45 mL). The Au(III) complex **B** (10 mg, 9 µmol) was transferred into a small glass vial and dissolved in *o*-dichlorobenzene (0.45 mL). Iodobenzene (19 µL, 0.17 mmol, 0.95 eq.) and methanol (18 µL) were added to the gold complex solution. This solution was loaded into a plastic syringe equipped with stainless steel needle. The syringe was closed by blocking the needle with a septum. Outside the glovebox, the Schlenk was cooled down to -10 °C (Ethanol/N_2 cold bath). At this temperature, the solution of gold complex and iodoarene was added. The reaction mixture was then stirred at 75 °C. Yield of **1** was determined using calibrated GC-MS with *n*-dodecane as internal standard.

Selected crystallographic data

Crystallographic data were collected at 193(2) K on a Bruker-AXS Kappa APEX II Quazar diffractometer equipped with a 30W air-cooled microfocus source using Mo K_α radiation (λ=0.71073 Å). Phi- and omega-scans were used. Space groups were determined on the basis of systematic absences and intensity statistics. Semi-empirical absorption correction was employed. [17] The structures were solved using an intrinsic phasing method (SHELXT), [18] and refined using the least-squares method on F^2. [19] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined isotropically at calculated positions using a riding model with their isotropic displacement parameters constrained to be equal to 1.5 times the equivalent isotropic displacement parameters of their pivot atoms for terminal sp^3 carbon and 1.2 times for all other carbon atoms. H atoms on Nitrogen were located by difference Fourier map and were freely refined. The triflate group of compound **23** was disordered over two positions, for which occupancies were refined. Several restraints (SAME, SIMU, DELU) were applied to refine this part of the molecule.

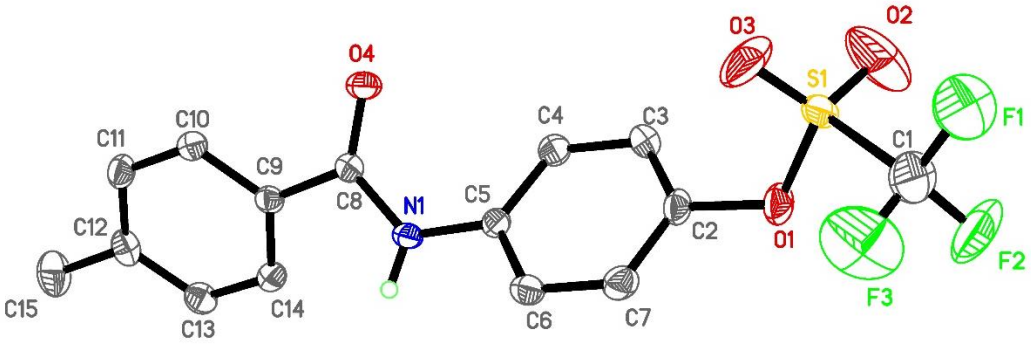
CCDC-1956358 (**13**) 1956359 (**23**) and 1956360 (**A.2LiOTf)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif.

Molecular structure of 13



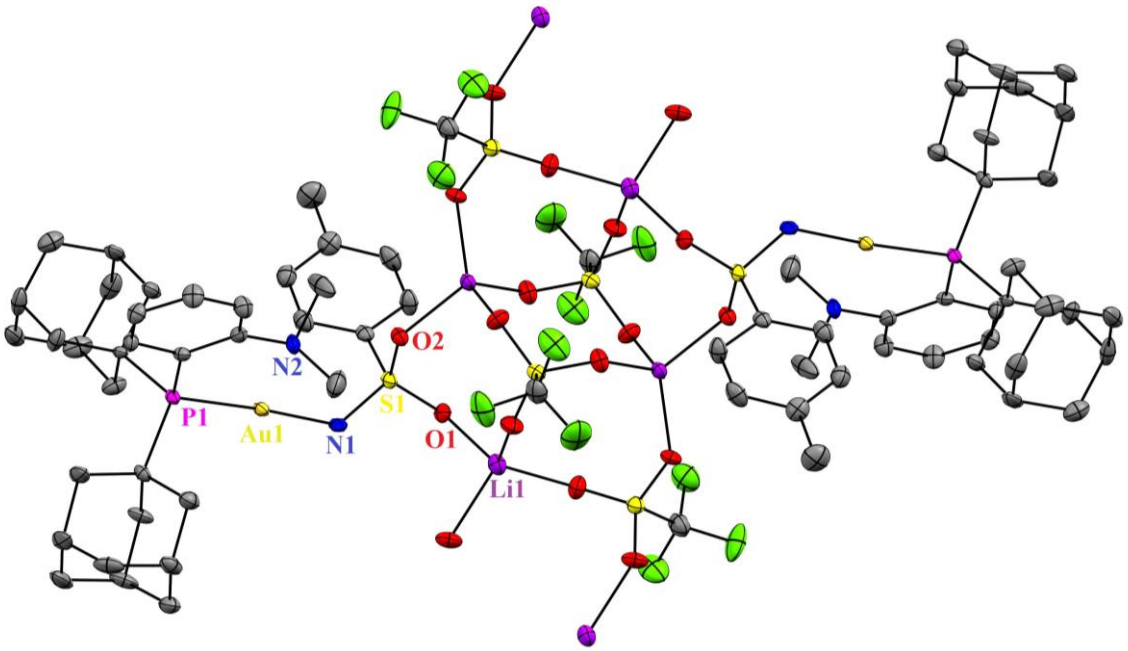
Molecular structure of **13**. Hydrogen atoms are omitted for clarity, except that on N; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°): O1-C8 1.2385(17), O2-B1 1.364(2), O2-C15 1.4655(18), O3-B1 1.359(2), O3-C16 1.4625(17), N1-C8 1.3473(19), N1-C5 1.4283(18), N1-H1 0.905(18), B1-C12 1.565(2), B1-O2-C15 107.39(12), B1-O3-C16 107.63(12), C8-N1-C5 126.52(12), C8-N1-H1 118.4(11), C5-N1-H1 115.0(11), O3-B1-O2 114.05(14), O3-B1-C12 122.92(15), O2-B1-C12 122.99(14).

Molecular structure of 23



Molecular structure of **23**. Disordered atoms and Hydrogen atoms are omitted for clarity, except that on N; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°): O1-C2 1.433(2), O1-S1 1.544(5), S1-O3 1.388(8), S1-O2 1.408(8), S1-C1 1.816(9), C1-F2 1.292(10), C1-F3 1.304(10), C1-F1 1.319(10), O4-C8 1.228(2), N1-C8 1.365(2), N1-C5 1.415(2), N1-H1 0.82(2), C2-O1-S1 119.6(3), O3-S1-O2 121.1(7), O3-S1-O1 112.6(7), O2-S1-O1 107.6(7), O3-S1-C1 108.6(7), O2-S1-C1 106.5(8), O1-S1-C1 97.8(5), F2-C1-F3 107.6(10), F2-C1-F1 111.5(11), F3-C1-F1 107.0(10), F2-C1-S1 111.6(8), F3-C1-S1 109.6(9), F1-C1-S1 109.4(10), C8-N1-C5 125.93(16), C8-N1-H1 118.0(15), C5-N1-H1 115.7(15)

Molecular structure of A.2LiOTf



Molecular structure of **A.2LiOTf**. It forms a 1D polymer in the solid state, the repetitive unit is shown here. Hydrogen atoms are omitted for clarity; thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (°): Au1-N1 2.038(5), Au1-P1 2.2453(14), N1-Au1-P1 175.37(15).

Table S5. Crystal Data, Data Collection, and Structure Refinement for **13, 23** and **A.2LiOTf**.

	13	**23**	**A.2LiOTf**
ID	AD220	JRV551	AD133
formula	$C_{20}H_{24}BNO_3$	$C_{15}H_{12}F_3NO_4S$	$C_{35}H_{48}AuN_2O_2PS$, 2 ($LiCF_3SO_3$)
M_r	337.21	359.32	1100.77
crystal system	monoclinic	triclinic	triclinic
space group	*P* $2_1/c$	*P* $\bar{1}$	*P* $\bar{1}$
a (Å)	10.2696(7)	5.2150(3)	9.8911(12)
b (Å)	18.4321(13)	8.2029(6)	14.4529(19)
c (Å)	9.8213(7)	18.0139(13)	17.441(2)
α (°)	90	80.189(3)	102.378(3)
β (°)	97.243(3)	84.276(2)	104.982(3)
γ (°)	90	89.238(2)	109.989(3)
V (Å^3)	1844.2(2)	755.54(9)	2133.9(5)
Z	4	2	2
ρ_{calc} (g cm^{-3})	1.214	1.579	1.713
μ (mm^{-1})	0.080	0.269	3.709
F(000)	720	368	1100
crystal size (mm^3)	0.70 x 0.08 x 0.06	0.60 x 0.20 x 0.06	0.20 x 0.08 x 0.02
T/K	193(2)	193(2)	193(2)
measd reflns	40581	19482	41545
Unique reflns (Rint)	4558 (0.0835)	3712 (0.0452)	9710 (0.0770)
Data / restraints / parameters	4558/0/235	3712/247/286	9710/1/548
GOF on F^2	1.048	1.056	1.027
R_1[a] [I>2σ(I)]	0.0501	0.0452	0.0482
wR_2[b] [all data]	0.1401	0.1184	0.0998
Largest diff. peak and hole e.Å^{-3}	0.352 and -0.246	0.361 and -0.264	1.360 and -1.980

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

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