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Supporting Information

Activation of a Metal-Halogen Bond by Halogen Bonding**

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Contents

1. Experimental Section

1.1. General Conditions

All experiments with moisture sensitive or oxygen sensitive compounds were carried out in flame dried *Schlenk* flasks under argon atmosphere and with dry solvents. Solvents used for column chromatography were previously distilled. All used chemicals are commercially available and were used without further purification unless noted further. Thin-layer chromatography was performed by using *Merck TLC aluminium sheets*. Column chromatography was performed with silica gel 60 F254 or Florosil® at atmospheric or slightly elevated (hand pump) pressure. The corresponding solvents, eluents and R_f values are listed at the corresponding experiment. Detection of the substances was achieved by fluorescence detection under UV light (wavelength $\lambda = 254$ nm).

1.2. Solvents

Dry DCM, diethyl ether and THF were received from a *MBRAUN MB SPS-800*. At first solvents were distilled, dried over 4 Å molecular sieve and finally dried on an Alox column. Further dry solvents were dried over flame dried 4Å molecular sieve. The moisture content was determined with a Karl Fischer *Titroline®7500KF trace*.

1.3. Chemicals

Chemicals were obtained from *ABCR*, *Alfa Aesar*, *Carbolution*, *Merck*, *ChemPur*, *Sigma Aldrich, TCI* or *VWR*. Commercially available reagents and starting materials were used without further purification (unless mentioned otherwise).

1.4. Analysis Methods

1.4.1. NMR Spectroscopy

^{1}H NMR spectra and ^{13}C NMR spectra were recorded with a *Bruker Avance III 300 NMR* or a *Bruker DPX-250 NMR* spectrometer at 298.5 K. ^{19}F NMR spectra were recorded with a *Bruker DPX-250 NMR* spectrometer at 298.5 K. ^{31}P NMR spectra were recorded with a *Bruker Avance III 400 NMR* or a *Bruker DPX-250 NMR* spectrometer at 298.5 K Peaks were referenced to residual ^{1}H signals from the deuterated solvents and are reported in parts per million (ppm). For ^{1}H NMR spectroscopic data and ^{19}F NMR spectroscopic data, multiplicity (s = singlet, d =

doublet, dd = doublet of doublet, t = triplet, p = pentet, m = multiplet), the relative integral and the coupling constant (*J* in *Hz*) are indicated.

1.4.2. ATR-IR Measurements

IR spectra were recorded with a *Shimadzu IR Affinity - 1S* spectrometer and are reported in $\nu = cm^{-1}$ and are indicated with w (weak), m (middle), s (strong) or vs (very strong).

1.5. ESI-MS Measurements

Mass spectra were recorded with a *Bruker Daltonics Esquire 6000* instrument.

1.6. Preparation of stock solutions

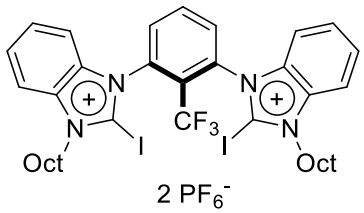
Chemicals for stock solutions and catalysis experiments were weighed out on a *Mettler Toledo XSR 105 Dual Range* balance. Liquid components were added using *Hamilton*® syringes. Stock solutions were sealed after preparation and stored at -30°C.

1.7. Synthesis of known compounds

Compounds **1a/b**[1], **2a/b**[1], **3a/b**[1], **4a**[2]**/b**[3], **6**[4] and **8**[5] were synthesized according to published literature procedures.

1.8. Synthesis of new compounds

1.8.1. Synthesis of 4c



2 g of Amberlyst® A-26 (OH) ion exchange resin were suspended in 15 ml of MeOH and cooled to 0°C. 2 ml of a 55% solution of HPF_6 in H_2O were added dropwise and the suspension was stirred for 30 minutes at 0°C. The mixture was warmed to room temperature and stirred for another 30 minutes at room temperature. The charged ion exchange resin was then filled into a thin glass column and washed with MeOH until the eluent showed neutral pH. The eluent was then changed to MeCN and the resin washed with an additional 50 ml of MeCN. 100 mg of triflate salt **4b** (0.086 mmol, 1 eq) were dissolved in 10 ml of MeCN and the solution was passed through the column in a span of 45 minutes. The received eluent was then again passed through the column in 30 minutes. Remaining product was eluted with 2 x 10 ml MeCN and the solvent

was removed under reduced pressure. The resulting residue was sonicated in the presence of pentane, the pentane was decanted and the solid dried under high vacuum, which yielded 99 mg of **4c** (0.086 mmol, quantitative yield) as a colorless solid.

(As minor decomposition in a sample stored under ambient conditions was observed over a period of several months, the product should be stored under argon, preferably at low temperature.)

^{1}H NMR (250 MHz, Acetonitrile-d$_3$):

δ [ppm] = 8.44 (t, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 8.08 – 8.00 (m, 2H), 7.83 – 7.61 (m, 6H), 4.64 (t, *J* = 7.5 Hz, 4H), 2.02 (m, 4H), 1.51-1.22 (m, 20H), 0.88 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (75 MHz, Acetonitrile-d$_3$):

δ [ppm] = 139.2, 137.1, 136.5, 135.1, 134.0, 129.4, 128.8, 127.3 (q, *J* = 31 Hz), 121.9 (q, *J* = 276 Hz), 114.7, 114.5, 52.2, 32.3, 29.7, 29.6, 29.5, 27.0, 23.3, 14.3.

^{19}F NMR (235 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = -56.3 (s, 3F, -C*F*$_3$), -72.9 (d, *J* = 706 Hz, 6F, P*F*$_6$).

^{31}P NMR (101 MHz, Acetonitrile-*d*$_3$):

δ [ppm] = -144.6 (sept, *J* = 706 Hz, *P*F$_6$,).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3119 (w), 2930 (w), 2859 (w), 1599 (w), 1589 (w), 1503 (w), 1477 (m), 1435 (w), 1404 (w), 1356 (w), 1287 (m), 1238 (w), 1177 (w), 1148 (w), 1043 (w), 1013 (w), 949 (w), 826 (vs), 752 (s), 679 (w), 617 (w), 556 (vs), 426 (w).

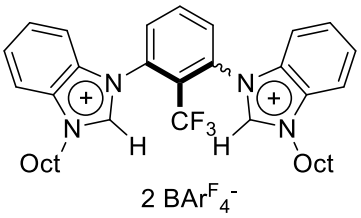
ESI-MS:

m/*z* (+) = calc. 875.17 $[M+F]^+$, 428.08 $[M]^{2+}$;

found 875.17 $[M+F]^+$, 428.11 $[M]^{2+}$.

m/*z* (-) = calc. 144.96 $[PF_6]^-$; found 144.63 $[PF_6]^-$.

1.8.2. Synthesis of 5a



The reaction was performed in a *CEM Discover SP* microwave using dynamic mode. 500 mg (554 µmol, 1 eq) of the corresponding triflate salt[6] were dissolved in 3 ml dry acetone in a 10 ml open microwave vessel, equipped with a small stirring bar. Subsequently, 982 mg (1.11 mmol, 2 eq.) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$) were added and the reaction vessel was placed in the microwave. The reaction mixture was heated for 2.5 hours to 45 °C in the microwave and after cooling to room temperature, the solvent was evaporated under reduced pressure. The residue was resuspended in a small amount of chloroform (3 ml) and purified using a small column packed with Florisil® (diameter 1 cm, height 15 cm). The resulting colorless oil was suspended in pentane and placed in an ultrasonic bath for 10 minutes. After removal of the solvent and drying under high vacuum, **5a** is obtained as slightly hygroscopic, off-white powder in 60 % yield (770 mg, 330 µmol).

The product is obtained as a mixture of two isomers (syn/anti) in a ratio of 40:60 (determined by ^{1}H NMR and ^{19}F NMR).

^{1}H NMR (300 MHz, Acetonitrile-d$_3$):

δ [ppm] = 9.25 (s, 1H, *major isomer*), 9.23 (s, 1H, *minor isomer*), 8.33 – 8.24 (m, 1H), 8.18 – 8.01 (m, 4H), 7.87 – 7.76 (m, 4H), 7.73 – 7.64 (m, 25H), 7.61 – 7.56 (m, 1H), 4.70-4.52 (m, 4H), 2.11 – 1.99 (m, 4H), 1.45 – 1.20 (m, 20H), 0.85 (m, 6H).
Overlap of signals is observed for syn/anti isomers.

^{13}C NMR (75 MHz, Acetonitrile-d$_3$):

δ [ppm] = 162.6 (q, *J* = 49.8 Hz), 142.4, 137.4, 135.6, 135.4, 134.5, 132.9, 131.8, 130.8, 130.5 130.1, 129.7, 129.0, 127.2, 123.6, 120.0, 118.63, 118.59, 115.2, 115.1, 114.5, 114.1, 49.2, 32.3, 29.7, 29.5, 26.9, 26.8, 23.2, 14.2.

Overlap of signals is observed for syn/anti isomers.

^{19}F NMR (235 MHz, Acetonitrile-d_3):

δ [ppm] = -55.7 (s, 1F, -CF_3, *minor isomer*), -55.9 (s, 2F, -CF_3, *major isomer*), -63.3 (s, 48F, $BAr^{F}{}_4^-$).

ATR-IR:

$\tilde{\nu}$ [cm^{-1}] = 3161 (w), 3100 (w), 2934 (w), 2862 (w), 1611 (w), 1562 (w), 1489 (w), 1462 (w), 1354 (s), 1273 (vs), 1113 (vs), 932 (w), 885 (m), 839 m(), 745 (m), 712 (s), 681 (s), 669 (s), 631 (w), 449 (w), 422 (w).

ESI-MS:

m/*z* (+) = calc. 1467.44 $[M- BAr^{F}{}_4]^+$, 302.19 $[M]^{2+}$;

found 1467.18 $[M- BAr^{F}{}_4]^+$, 302.55 $[M]^{2+}$.

m/*z* (-) = calc. 863.07 $[BAr^{F}{}_4]^-$; found 862.70 $[BAr^{F}{}_4]^-$.

2. Catalysis experiments

2.1. General procedure for cyclization of 6

An NMR tube was evacuated for 10 minutes and refilled with argon. Then, 300 µL of a 133 mM solution of propargylic amide **6** (6.53 mg, 40 µmol, 1 eq) and tetraethylsilane (1.9 µL, 10 µmol, 0.25 eq) in $CDCl_3$ were added. Subsequently, 100 µL of an 8 mM solution of the activator (0.8 µmol, 0.02 eq) in $CDCl_3$ were added and finally, 100 µL of an 8 mM solution of $(PPh_3)AuCl$ (0.8 µmol, 0.02 eq) in $CDCl_3$ were added to the mixture. The NMR tube was sealed and mixed thoroughly by inversion. Periodic ^1H NMR measurements were used to determine the conversion of amide **6**.

In cases where the added activator suffered from poor/incomplete solubility in $CDCl_3$, the activator was weighed in directly and 100 µL of $CDCl_3$ were added to account for equal reaction volume.

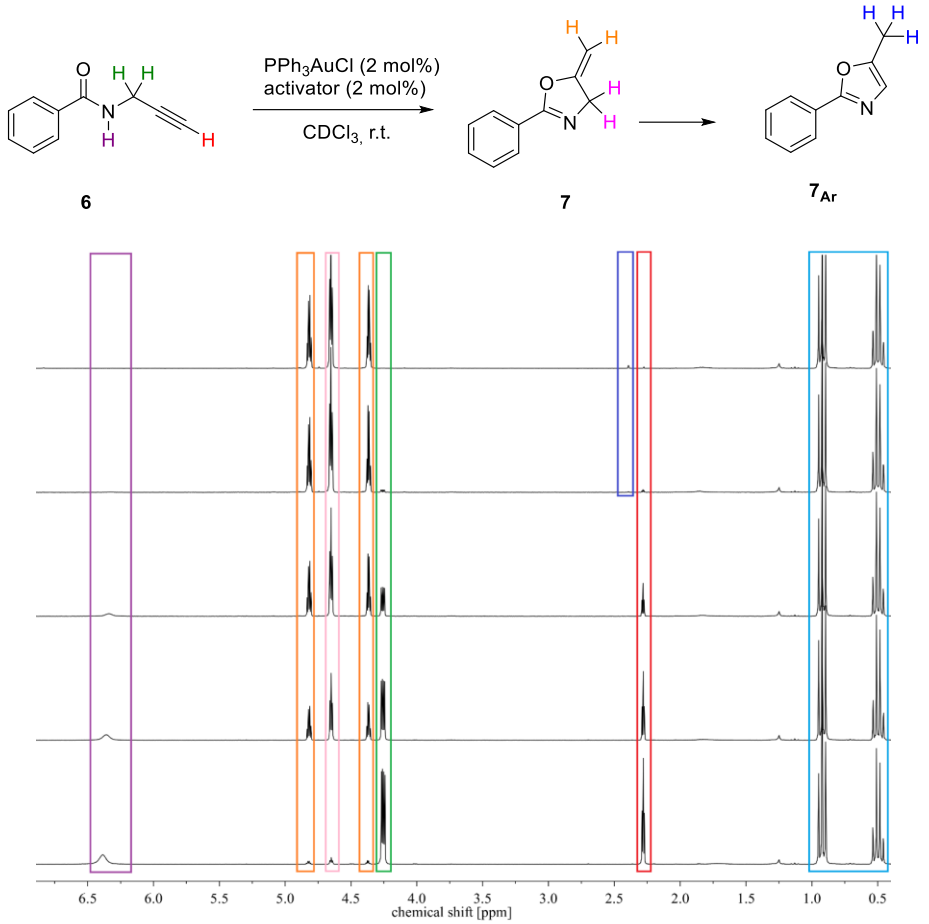


Figure S1: Stacked ^{1}H NMR spectrum of the Au-catalyzed cyclization of **6** with **1a** as additive. The protons of the tetraethylsilane standard are marked in light blue, the alkyne proton of the reactant **6** is marked in red, the propargyl CH_2 protons of the reactant are marked green and the amide proton of the reactant is marked violet. The CH_2 ring proton signals of the oxazoline product **7** are marked in pink and the alkene protons of product **7** are marked in orange. The emerging methyl proton signal of the aromatization product $\mathbf{7}_{Ar}$ is marked in dark blue.

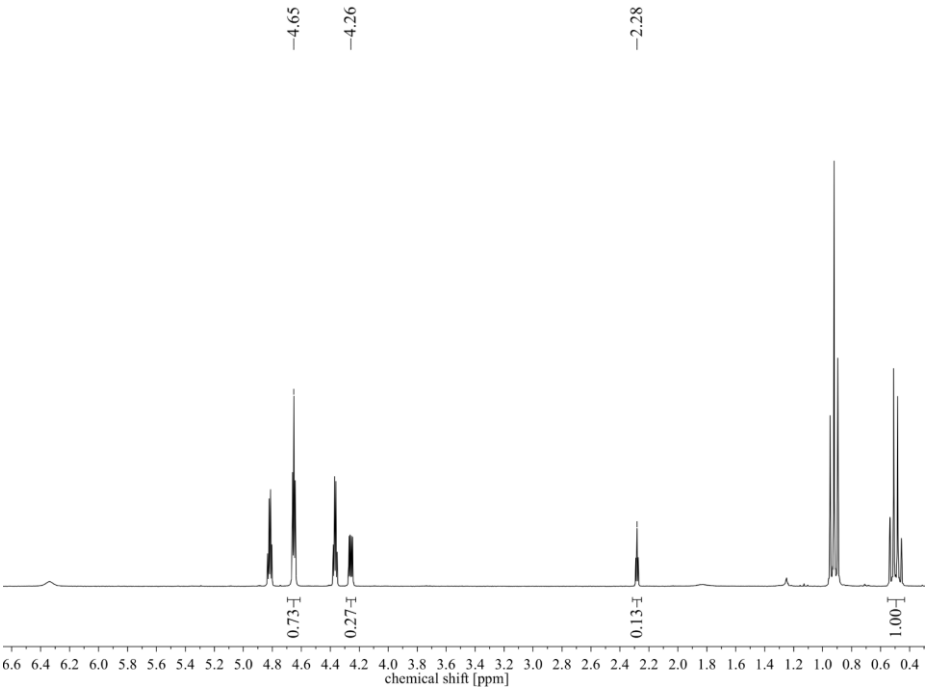


Figure S2: ^{1}H NMR spectrum of the Au-catalyzed cyclization of **6** with **1a** as additive during ongoing reaction. The determination of conversion is shown exemplarily, with the integral of CH_2 protons of the TES standard set to 1, the attenuation of the reactant signals at 2.28 ppm and 4.26 ppm was followed with the conversion being easily deductible from the integration of the signal at 4.26 ppm. Cross reference was possible by comparison of the ratio of the reactant and product signal integrals at 4.26 and 4.65 ppm, with the conversion in this case being 73%.

2.2. General procedure for cyclization of 8

An NMR tube was evacuated for 10 minutes and refilled with argon. Then, 300 µL of a 133 mM solution of malonate ester **8** (9.53 mg, 40 µmol, 1 eq) and tetraethylsilane (1.9 µL, 10 µmol, 0.25 eq) in $CDCl_3$ were added. Subsequently, 50 µL of an 8 mM solution of the activator (0.4 µmol, 0.01 eq) in $CDCl_3$ were added as well as 100 µL of $CDCl_3$. Finally, 50 µL of an 8 mM solution of $(PPh_3)AuCl$ (0.4 µmol, 0.01 eq) in $CDCl_3$ were added to the mixture. The NMR tube was sealed and mixed thoroughly by inversion. Periodic ^{1}H NMR measurements were used to determine the yield of cyclization products **9a/b**.

In cases where the added activator suffered from poor/incomplete solubility in $CDCl_3$, the activator was weighed in directly and 50 µL of $CDCl_3$ were added to account for equal reaction volume.

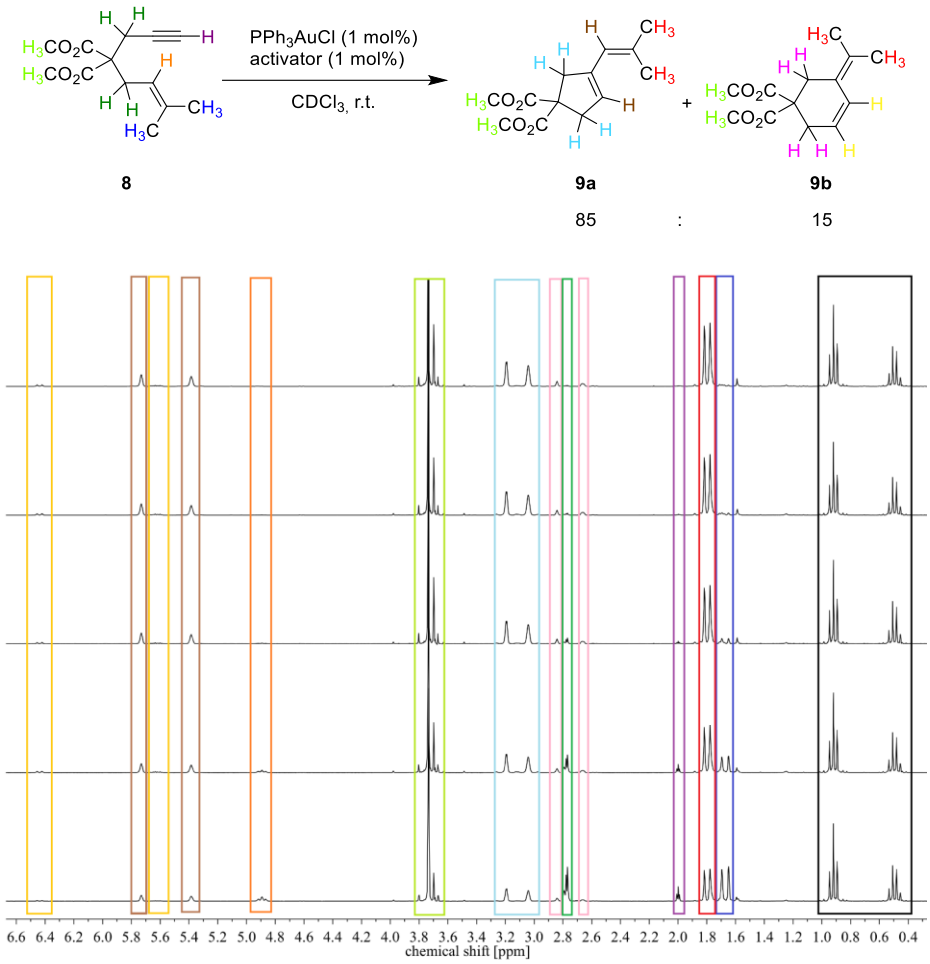


Figure S3: Stacked ^{1}H NMR spectrum of the Au-catalyzed cyclization of **8** with **1a** as additive. The protons of the tetraethylsilane standard are marked in black, the reactant allylic methyl proton signal is marked in dark blue, while the overlapping product allylic methyl proton signals are marked in red. The reactant alkyne CH proton signal is marked in violet. The signal of the propargylic CH_2 protons of the reactant and the allylic CH_2 protons of the reactant are marked in green, while CH_2 signals from the product ring systems are marked in pink and light blue respectively. Overlapping reactant/product signals of the methyl ester protons are marked in light green. The alkene proton from reactant **8** is marked in orange, while the resulting alkene protons of the products **9a/b** are in the range marked in brown and yellow respectively (see Figure S5 for details).

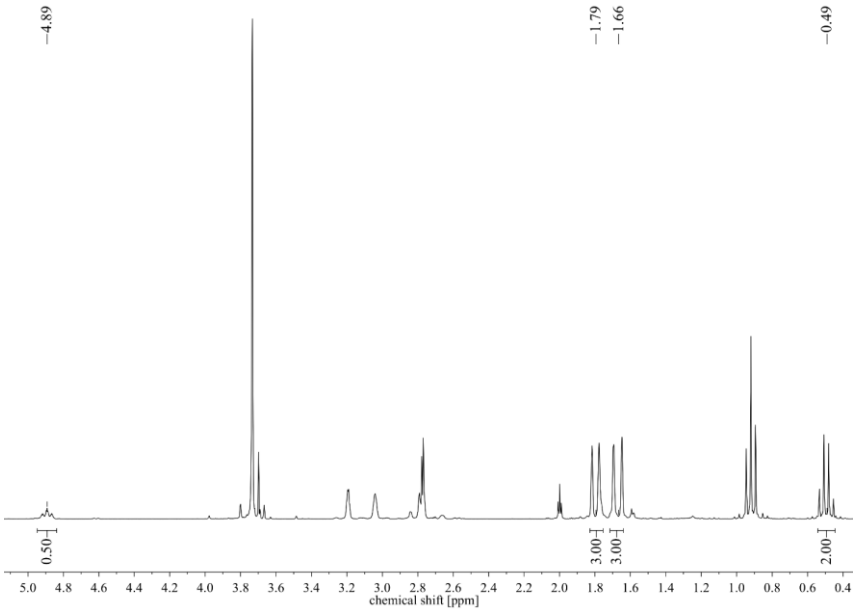


Figure S4: ^{1}H NMR spectrum of the Au-catalyzed cyclization of **8** with **1a** as additive. The determination of yield is shown exemplarily. The integral of the CH_2 signal of the tetraethylsilane internal standard is set to 2, and the ratio of reactant to product is determined by comparison of the methyl signals at 1.66 ppm and 1.79 ppm. Cross reference is possible by checking the attenuation of any number of reactant signals, conveniently the isolated proton signal at 4.89 ppm. The yield in this case is 50%.

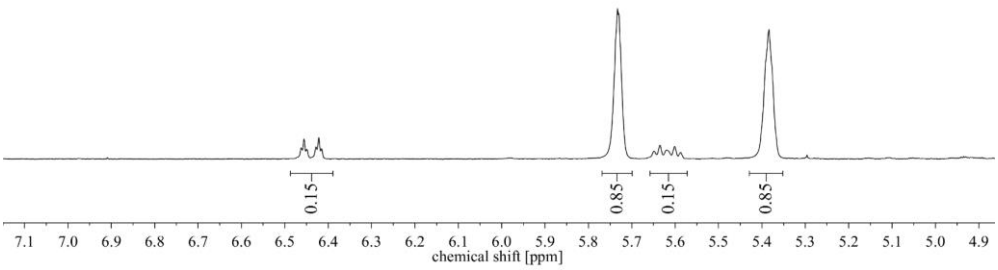


Figure S5: ^{1}H NMR spectrum of the Au-catalyzed cyclization of **8** with **4a** as additive after completed reaction. The determination of product ratio is exemplarily shown here, determined by comparison of the integration of alkene proton signals of **9a** (5.74 ppm, 5.39 ppm) and **9b** (6.44 ppm, 5.62 ppm)[7]. In this case, the product ratio observed is 85:15, which was found for all additives which generated significant conversion.

2.3. Additional kinetic data for cyclization of 6

Table S1. Cyclization of **6** in the presence of activators and reference compounds.

Entry	Activator	Conversion after 3 h [%]	Conversion after 12 h [%]	Conversion after 21 h [%]
1	None	≤5	≤5	≤5
2	**1a**	60	98	>99
3	**1b**	≤5	≤5	≤5
4	**2a**	38	90	98
5	**2b**	≤5	≤5	≤5
6	**3a**	≤5	≤5	≤5
7	**3b**	≤5	≤5	≤5
8	**4a**	92	99	>99
9	**4b**	≤5	≤5	≤5
10	**4c**	25	69	91
11	**5a**	≤5	18	43
12	$NaBAr^{F}_{4}$	95	>99	>99
13	$TMABAr^{F}_{4}$	≤5	≤5	≤5
14	AgOTf	5	13	21
15	$AgBF_4$	14	87	>99
16	$AgPF_6$	44	>99	>99
17	1 mol% I_2	≤5	≤5	≤5
18	1 mol ‰ I_2	≤5	≤5	≤5

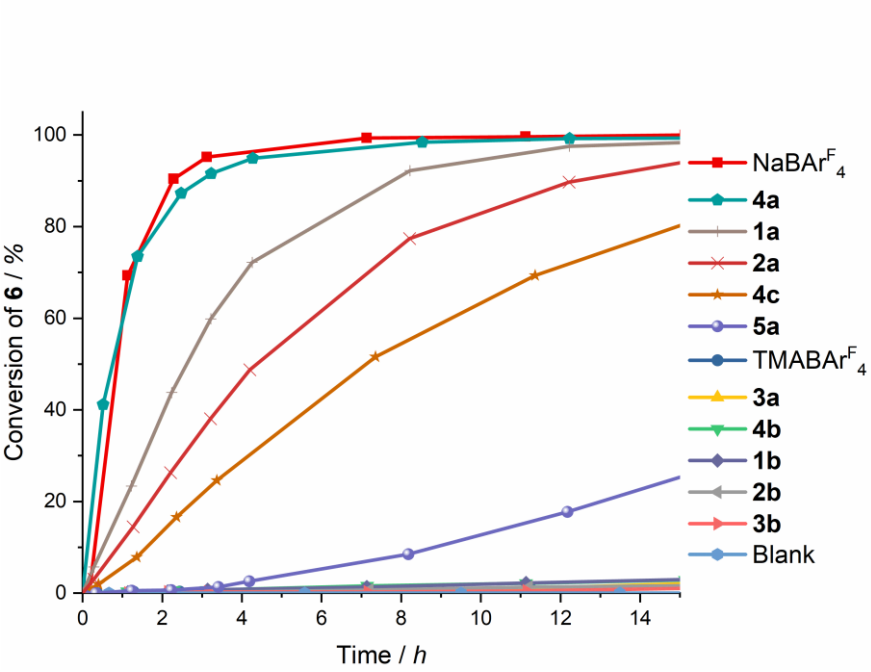


Figure S6: Extended kinetic plot for different activators in cyclization of **6**.

2.4. Additional kinetic data for cyclization of 8

Table S2. Cyclization of **8** in the presence of 1 mol% of activators and reference compounds.

Entry	Activator	Conversion after 40 minutes [%]	Conversion after 2 h [%]	Conversion after 15 h [%]
1	None	≤5	≤5	≤5
2	**1a**	76	89	96
3	**1b**	≤5	≤5	8
4	**2a**	43	60	82
5	**2b**	≤5	≤5	6
6	**3a**	≤5	≤5	≤5
7	**3b**	≤5	≤5	≤5
8	**4a**	83	94	97
9	**4b**	≤5	≤5	≤5
10	**5a**	≤5	9	24
11	NaBAr$^F_4$	84	97	>99
12	TMABAr$^F_4$	≤5	≤5	≤5

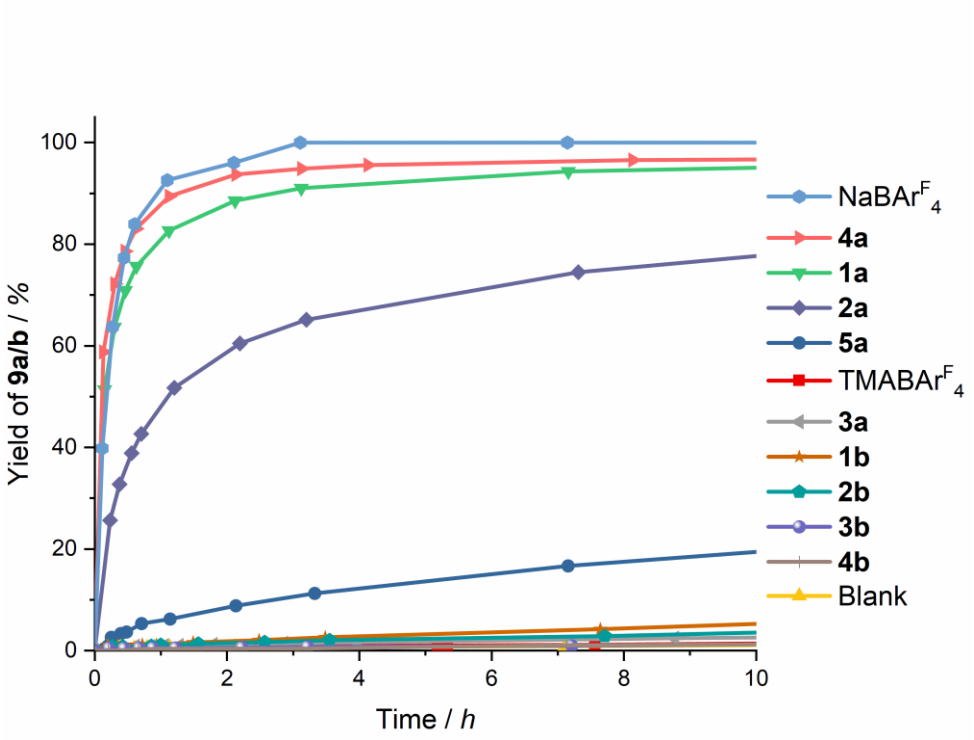


Figure S7: Extended kinetic plot for activators in cyclization of **8**.

2.5. Determination of k_{rel} values

Relative rate accelerations (k_{rel} values) were derived from the kinetic plots of the reactions. For a set reaction time (70 minutes for cyclization of **6**, 20 minutes for cyclization of **7**) a conversion/time slope was determined. For this, the corresponding conversion at the given time was divided by the reaction time to yield a slope of arbitrary unit.

The conversion/time slope of addition of **3a** was set as benchmark (k_{rel} = 1), with the given k_{rel} values representing multiples of the initial rate derived through experiments by addition of **3a**.

3. Additional NMR spectra

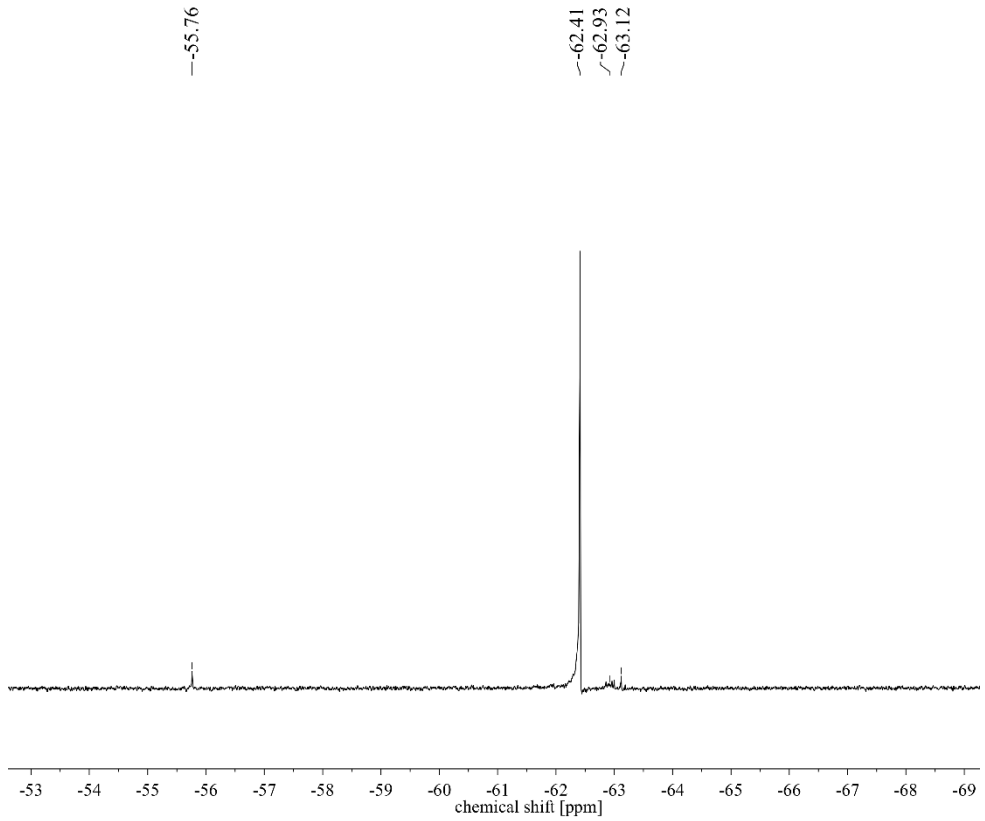


Figure S8: ^{19}F NMR spectrum of the reaction mixture of a cyclization of **6** with 2 mol% of XB donor **4a** added after 15 hours of reaction time. Visible are the single signal of the CF_3 fluorine atoms at -55.76 ppm which indicates the stability of the XB donor, and the signal of the BAr^F_4 anion at -62.41 ppm accompanied by small peaks derived from decomposition[8] of the BAr^F_4 anion around -62.93 ppm and -63.12 ppm (cf. figures S9, S10).

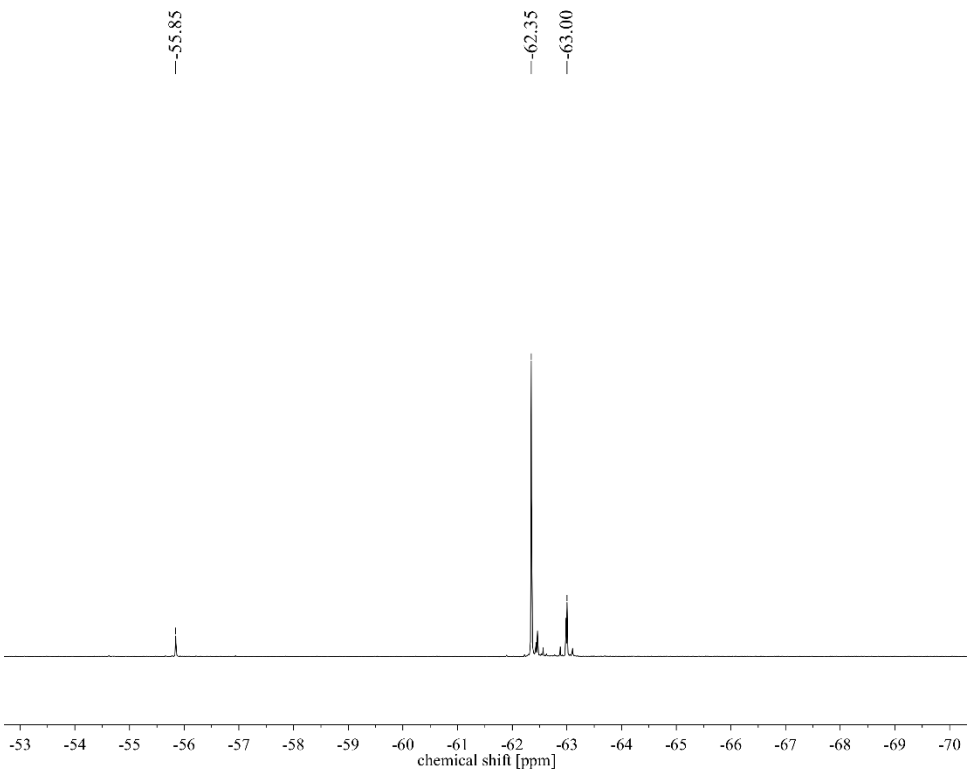


Figure S9: ^{19}F NMR spectrum of a 1:1 mixture of XB donor **4a** and $(PPh_3)AuCl$ in $CDCl_3$, 5 hours after mixing. For the XB donor, again only a single signal is visible at -55.85 ppm. In this case, increased decomposition of the $BAr^F{}_4$ anion is observed, likely due to much higher concentration of the cationic gold species.

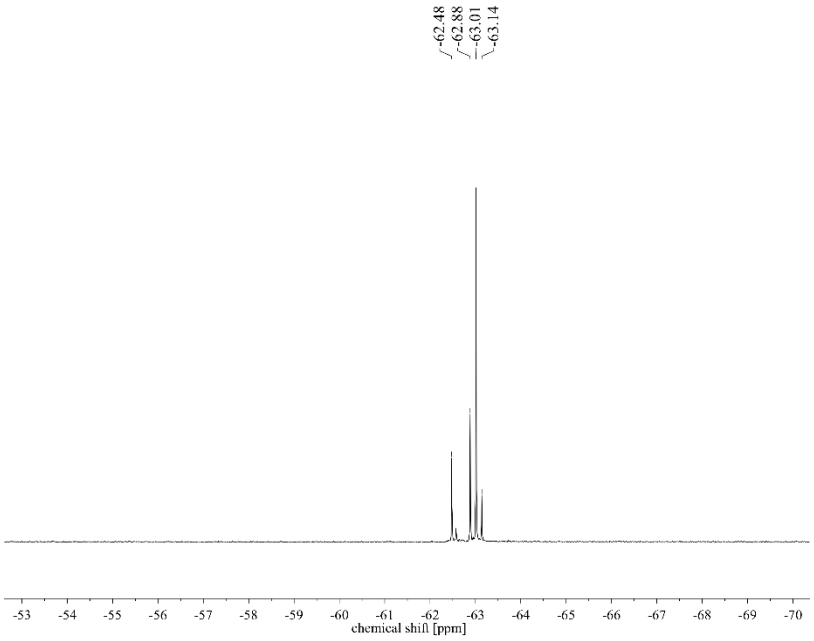


Figure S10: ^{19}F NMR spectrum of a 1:1 mixture of $NaBAr^F{}_4$ and $(PPh_3)AuCl$ in $CDCl_3$, a week after mixing, showing extensive decomposition of the $BAr^F{}_4$ anion, possibly by activation of the B-C bonds by the cationic gold complex.[8]

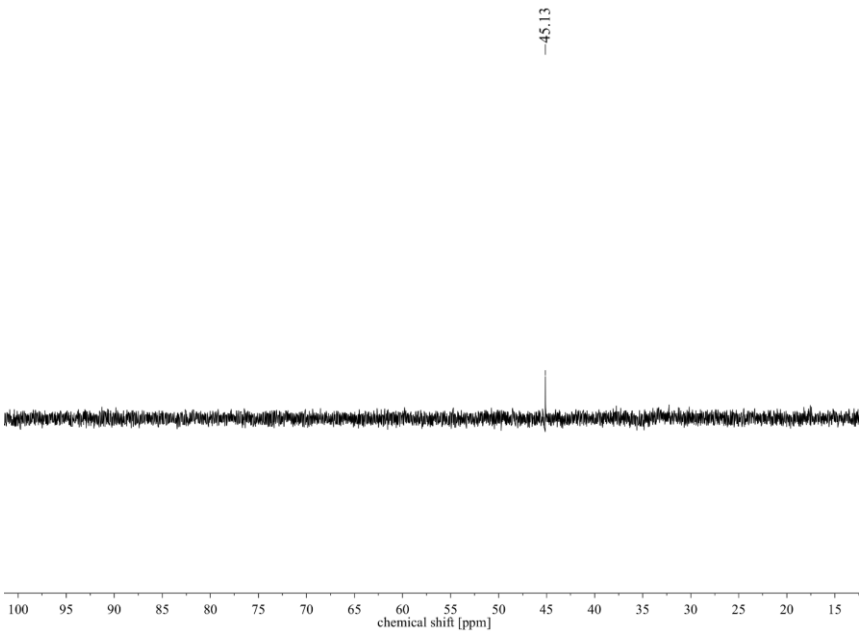


Figure S11: ^{31}P NMR spectrum of a 1:1 mixture of XB donor **4a** and $(PPh_3)AuCl$ in $CDCl_3$.

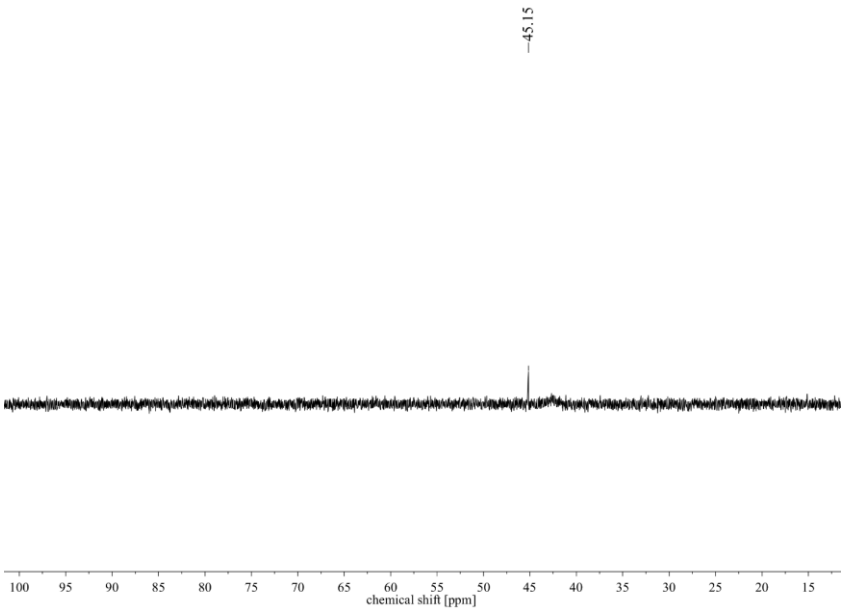


Figure S12: ^{31}P NMR spectrum of a 1:1 mixture of $NaBAr^F{}_4$ and $(PPh_3)AuCl$ in $CDCl_3$.

4. DFT Calculations

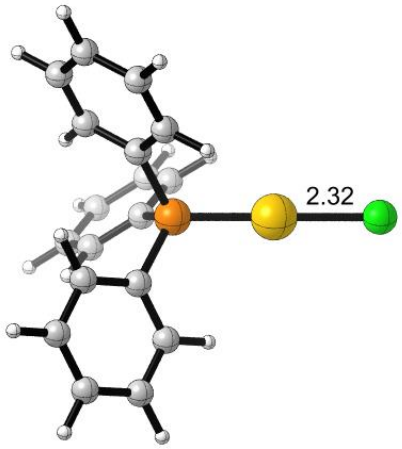
DFT calculations were performed on the adducts between (PPh_3)AuCl and a truncated version of halogen bond donor **4a**, in which the octyl groups were replaced with methyl and the counterions were omitted. For the calculations, the Gaussian16 suite of programs was used (Revision B.01).[9] To this end, the M06-2X functional[10] was used with the def2-TZVP basis set on all atoms except gold, chlorine and iodine, which were treated with def2-TZVPD including the corresponding pseudopotential.[11] In addition, Grimme D3(0) dispersion corrections[12] were applied and in parallel to gas phase calculations, all structures were also treated with the SMD18 intrinsic solvation model.[13] All minima were confirmed by frequency calculations, which yielded no imaginary frequencies. The coordinates and energies (in hartree) of the structures are given below.

(PPh_3)AuCl (gasphase)

E = -1632.177208

H = -1631.877993

G = -1631.952278



Cl	-4.15165500	0.00076100	0.00186700
Au	-1.83293300	0.00140800	0.00090800
P	0.39275400	0.00016000	-0.00044600
C	1.12708200	-1.36547800	-0.94901400
C	2.28534600	-1.20747400	-1.70584000
C	0.51679200	-2.61703900	-0.87557200
C	2.83065000	-2.29456100	-2.37572500
H	2.75913200	-0.23646700	-1.78001900
C	1.06887700	-3.70129500	-1.53922000
H	-0.39738500	-2.73727800	-0.30541300

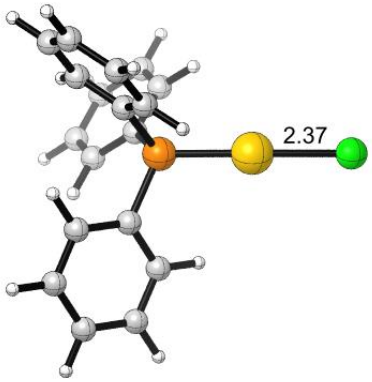
C	2.22624900	-3.54047100	-2.29023600
H	3.72718800	-2.16477800	-2.96762200
H	0.58863100	-4.66893600	-1.47925200
H	2.65154200	-4.38546900	-2.81585400
C	1.13015800	1.50339500	-0.70839800
C	2.29340700	2.07262500	-0.19636300
C	0.51785300	2.07190600	-1.82478600
C	2.84190300	3.19522700	-0.80203500
H	2.76909400	1.64646000	0.67826000
C	1.07298300	3.18786200	-2.43106200
H	-0.39976600	1.64372700	-2.21192200
C	2.23536700	3.75051900	-1.91960800
H	3.74251900	3.63704100	-0.39627800
H	0.59125000	3.62450800	-3.29583900
H	2.66325500	4.62729500	-2.38799900
C	1.13014000	-0.13942500	1.65548000
C	2.28697700	-0.87678300	1.89468900
C	0.52421200	0.55230200	2.70369400
C	2.83526200	-0.91403800	3.16982500
H	2.75745000	-1.42832600	1.09008200
C	1.07935000	0.51906200	3.97316200
H	-0.38828300	1.10957500	2.52485300
C	2.23532200	-0.21457500	4.20704100
H	3.73061100	-1.49397500	3.35153800
H	0.60262900	1.05692300	4.78188400
H	2.66307400	-0.24743800	5.20059600

(PPh$_3$)AuCl (chloroform)

E = -1632.213377

H = -1631.914342

G = -1631.987935



Cl	4.18389100	-0.00537600	0.01005200
Au	1.81540700	-0.00379300	0.00679000
P	-0.41549800	-0.00042300	0.00022900

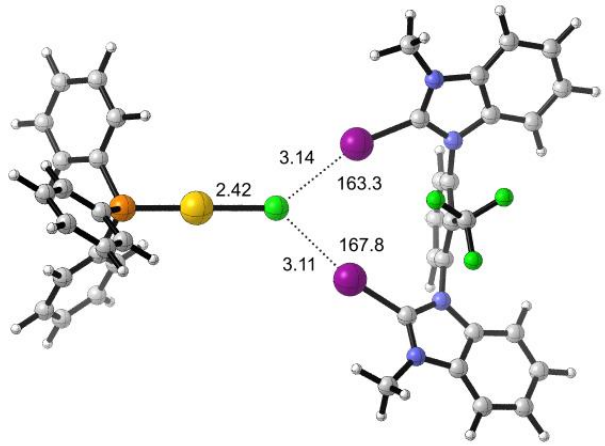
C	-1.14230400	-0.19620200	1.65339900
C	-2.27655800	0.50610200	2.05267700
C	-0.55127300	-1.11015700	2.52628200
C	-2.81671600	0.29094500	3.31438100
H	-2.73896500	1.22396500	1.38629100
C	-1.09886500	-1.32787700	3.78105100
H	0.34067100	-1.64751200	2.22312800
C	-2.23168300	-0.62612200	4.17628600
H	-3.69542000	0.84322100	3.62211000
H	-0.63565800	-2.03802600	4.45391700
H	-2.65369900	-0.78999100	5.15972900
C	-1.12598900	1.53527600	-0.66064300
C	-2.26395000	1.54123500	-1.46345400
C	-0.51696200	2.74177700	-0.31472100
C	-2.78972400	2.74638700	-1.91173100
H	-2.74051900	0.61028600	-1.74528500
C	-1.05013700	3.94246600	-0.75733600
H	0.37783800	2.73845500	0.29801700
C	-2.18654400	3.94515700	-1.55756800
H	-3.67128800	2.74565000	-2.53998500
H	-0.57247000	4.87508700	-0.48587800
H	-2.59715300	4.88273100	-1.91031500
C	-1.13254300	-1.33491600	-1.00148700
C	-2.28943000	-2.00868200	-0.61723400
C	-0.51277000	-1.65689100	-2.20901800
C	-2.82330700	-2.99320400	-1.43881600
H	-2.77418100	-1.77235200	0.32226600
C	-1.05395200	-2.63448200	-3.02973300
H	0.39648100	-1.14374700	-2.50258200
C	-2.20927000	-3.30403800	-2.64424500
H	-3.71954500	-3.51799000	-1.13353200
H	-0.56836800	-2.87989300	-3.96546700
H	-2.62663800	-4.07317600	-3.28169800

Complex of "4a" with (PPh_3)AuCl (gasphase)

E = -3632.225804

H = -3631.530487

G = -3631.681257



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C	4.53362200	1.11514800	-1.11249100
C	4.43995700	-1.26682600	-1.13159700
C	4.39023400	-1.25157500	-2.51886100
C	4.48259000	1.13886300	-2.49559900
H	4.29967700	-2.19188900	-3.04737500
H	4.46782700	2.09358000	-3.00548800
C	3.40725900	2.99858400	0.02067000
N	3.75159200	4.17973400	0.52550100
C	3.19042200	-3.00338300	0.09486500
N	3.44011800	-4.20306400	0.61288900
I	1.51713600	2.16833100	-0.08911200
I	1.41113800	-1.94367300	0.12218100
C	2.87862600	5.18046000	1.12757200
H	3.18946400	5.34743500	2.15732500
H	1.85398300	4.82389700	1.10704300
H	2.95775400	6.10641500	0.56079300
C	2.51519600	-5.07453500	1.32727600
H	2.90987400	-5.26750700	2.32319600
H	2.41299900	-6.01016300	0.78033800
H	1.54902300	-4.58661000	1.40439400
H	4.39703000	-0.03961300	-4.28512300
C	5.62139300	3.20010600	-0.21423800
C	5.12995900	4.34692000	0.39716500
C	5.32855500	-3.47885000	-0.34124400
C	4.76943500	-4.53962400	0.36182000
N	4.51766500	2.37137000	-0.42389400
N	4.31147400	-2.53747300	-0.48962300
C	5.96267900	5.39753500	0.76160500
C	7.30551500	5.23892700	0.47843500
H	7.99647200	6.02811300	0.74057600

C	7.79915300	4.07982500	-0.14050700
H	8.85913100	4.00370400	-0.33987200
C	6.96915400	3.03473800	-0.49853100
C	6.65563200	-3.47926800	-0.74707900
C	7.39186400	-4.60177300	-0.41832700
H	8.43123500	-4.65555300	-0.71147400
C	6.82818500	-5.67644700	0.28674200
H	7.44621000	-6.53265200	0.51902400
C	5.50734100	-5.66915800	0.69238500
H	5.58463000	6.29078700	1.23939700
H	7.34742100	2.13736400	-0.96863600
H	7.08789000	-2.64958100	-1.28962900
H	5.07632700	-6.49764200	1.23735000
C	4.76518800	-0.03527900	1.10713800
F	5.85462800	0.68269400	1.38560800
F	4.93386300	-1.23620500	1.65139800
F	3.73623000	0.54337500	1.72820800
Cl	-0.88455900	0.15093700	-0.04719100
Au	-3.30419100	0.08343000	-0.02447100
P	-5.54571200	0.01248100	-0.01636200
C	-6.23725300	-0.11686400	1.65012100
C	-7.41047200	0.54847900	1.99847600
C	-5.61035500	-0.95162900	2.57480700
C	-7.95204500	0.37452600	3.26489400
H	-7.90029800	1.20266700	1.28792100
C	-6.15919900	-1.12662800	3.83464200
H	-4.69320100	-1.46420600	2.30698300
C	-7.33000600	-0.46249800	4.17996100
H	-8.86140300	0.89463700	3.53473200
H	-5.67235200	-1.77619700	4.54970900
H	-7.75516800	-0.59541800	5.16599500
C	-6.29114800	1.48662200	-0.75481700
C	-7.36961600	1.39731600	-1.63057600
C	-5.79965900	2.73765500	-0.38092600
C	-7.95261200	2.55618500	-2.12701600
H	-7.75553700	0.43026900	-1.92760800
C	-6.39067300	3.88941100	-0.87236700
H	-4.95797500	2.80793300	0.29929100
C	-7.46701900	3.79845400	-1.74748000
H	-8.78878700	2.48482300	-2.80962300
H	-6.01169200	4.85860000	-0.57679500
H	-7.92536500	4.69879200	-2.13475600
C	-6.19136300	-1.39838400	-0.94716100
C	-7.27487200	-2.14036700	-0.48443100
C	-5.61874000	-1.69920700	-2.18323900
C	-7.78263100	-3.17567500	-1.25856000
H	-7.72225600	-1.91609800	0.47577900
C	-6.13504700	-2.72719900	-2.95454300
H	-4.77212800	-1.12468700	-2.54268500
C	-7.21701700	-3.46666000	-2.49113700
H	-8.62293200	-3.75264100	-0.89623900

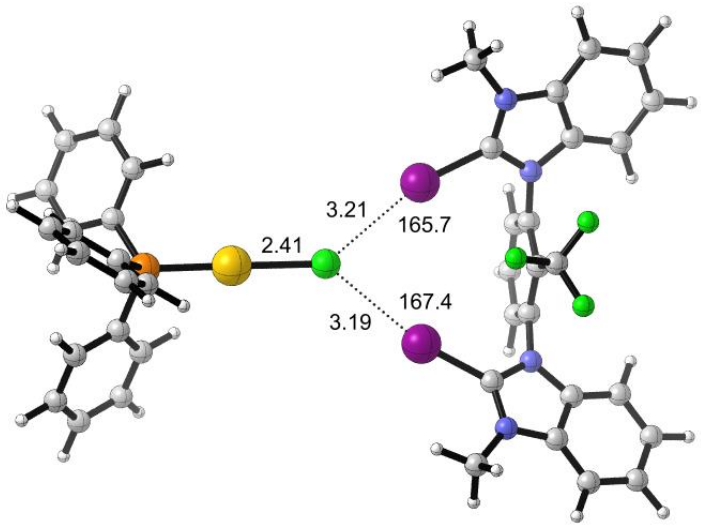
H	-5.69303400	-2.95479400	-3.91536300
H	-7.61736500	-4.27230000	-3.09231900

Complex of "4a" with (PPh_3)AuCl (chloroform)

E = -3632.414568

H = -3631.71947

G = -3631.865465



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C	-4.46798900	1.22229900	-1.12273500
C	-4.33316100	1.22031400	-2.50200600
C	-4.36944000	-1.17178200	-2.49331100
H	-4.22770700	2.16520800	-3.01936900
H	-4.29655600	-2.12314800	-3.00457500
C	-3.39229800	-3.01185800	0.07419300
N	-3.72126500	-4.20295200	0.56005300
C	-3.28520400	3.00330500	0.10874800
N	-3.56054000	4.20696900	0.59669100
I	-1.52797400	-2.12558700	0.04423700
I	-1.47338400	2.01098300	0.13979700
C	-2.85208900	-5.18197000	1.19980100
H	-3.26325500	-5.42389000	2.17781400
H	-1.85701200	-4.76479200	1.31564400
H	-2.81047200	-6.07567100	0.57993800
C	-2.66748900	5.11926600	1.29820900
H	-3.03342100	5.25705700	2.31403600
H	-2.65772300	6.07091700	0.77066000
H	-1.66535400	4.70334900	1.32064900
H	-4.20292800	0.01588500	-4.26850100
C	-5.57000800	-3.28574400	-0.30045300

C	-5.08028800	-4.41444400	0.34542400
C	-5.42635600	3.41403500	-0.34578200
C	-4.89400700	4.50309500	0.33388000
N	-4.48780200	-2.42253600	-0.44295300
N	-4.39256400	2.48875800	-0.46007900
C	-5.90170800	-5.48871100	0.66532300
C	-7.22897800	-5.37001200	0.30088100
H	-7.91114400	-6.17845700	0.52672800
C	-7.72026800	-4.22782300	-0.35275600
H	-8.76890400	-4.18447100	-0.61457400
C	-6.90277000	-3.15900000	-0.66604800
C	-6.75085600	3.37551700	-0.75969600
C	-7.51152600	4.48956400	-0.46051800
H	-8.55034600	4.51412700	-0.76070500
C	-6.97510600	5.59171500	0.22568800
H	-7.61431700	6.43795900	0.43874400
C	-5.65708900	5.62343500	0.63868900
H	-5.52244000	-6.36662400	1.17086100
H	-7.27385800	-2.27358800	-1.16435300
H	-7.15812900	2.52103100	-1.28341800
H	-5.24154800	6.46782800	1.17191500
C	-4.85371900	0.02982500	1.09840800
F	-5.63234000	-0.98897400	1.46399500
F	-5.45987700	1.14042000	1.51596500
F	-3.70981800	-0.07937600	1.78198900
Cl	0.94006200	-0.07720200	0.00458200
Au	3.35268400	-0.05603700	-0.00461700
P	5.58691600	-0.00989800	-0.02836400
C	6.31992500	-0.15398700	1.62284900
C	7.50355200	-0.85595600	1.83774300
C	5.69630400	0.49940000	2.68568800
C	8.05957900	-0.89960400	3.10960700
H	7.99256800	-1.36933500	1.01880000
C	6.25941400	0.45840600	3.95175900
H	4.76854300	1.03626900	2.52042700
C	7.44079100	-0.24234200	4.16407000
H	8.97805900	-1.44808000	3.27431800
H	5.77286500	0.96701900	4.77400300
H	7.87626400	-0.27903500	5.15452000
C	6.31411100	-1.34717300	-1.01363900
C	7.40272800	-1.13130500	-1.85445000
C	5.78034700	-2.62940800	-0.88297100
C	7.95401900	-2.19486700	-2.55802500
H	7.82091000	-0.13848400	-1.96660600
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H	4.92714600	-2.79687400	-0.23461600
C	7.42658800	-3.47076600	-2.41969900
H	8.79722100	-2.02239900	-3.21442000
H	5.92546600	-4.68257200	-1.47339500
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C	7.36856400	2.15387800	-0.22222800
C	5.59385900	2.06311500	-1.85392200
C	7.85895000	3.30319800	-0.82906700
H	7.87046900	1.75095100	0.64888100
C	6.09250200	3.20508100	-2.46087100
H	4.70443400	1.58220300	-2.24695800
C	7.22518600	3.82628800	-1.94744400
H	8.73848100	3.78818900	-0.42556000
H	5.59444700	3.61404700	-3.33056400
H	7.61082000	4.72159700	-2.41831600

Truncated cation of 4a (gasphase)

E = -1999.987854

H = -1999.593784

G = -1999.68606

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C	-1.19298800	0.19675300	1.12775800
C	-1.19618500	-0.21532300	2.45181400
C	1.19605300	-0.21537800	2.45189700
H	-2.14403000	-0.35036800	2.95700800
H	2.14385300	-0.35046700	2.95715300
C	3.29891600	-0.43381300	-0.03001400
N	4.35787200	0.19356600	-0.53091100
C	-3.29892300	-0.43380600	-0.03004600
N	-4.35791700	0.19352400	-0.53092200
I	2.94211700	-2.44948200	-0.08553000
I	-2.94209200	-2.44947700	-0.08535900
C	5.51764700	-0.38352300	-1.20603000
H	5.56931200	0.01476800	-2.21762200
H	5.41960000	-1.46333500	-1.24123000
H	6.41522800	-0.11469700	-0.65219400
C	-5.51776200	-0.38362600	-1.20586600
H	-5.56989900	0.01511000	-2.21725700
H	-6.41523800	-0.11533700	-0.65160400
H	-5.41937000	-1.46338200	-1.24161300
H	-0.00013900	-0.75763900	4.14579300
C	3.00459700	1.73979800	0.35343000
C	4.21198700	1.56222100	-0.31127500
C	-3.00458400	1.73984600	0.35318900
C	-4.21203800	1.56219300	-0.31139100
N	2.45915900	0.46464700	0.51582000
N	-2.45913200	0.46471100	0.51564500
C	5.03870000	2.63245300	-0.63200500
C	4.59046700	3.88229400	-0.25331000
H	5.19548100	4.74967600	-0.47848600

C	3.37110200	4.05959300	0.42103800
H	3.06898800	5.05963100	0.69996700
C	2.55257800	2.99414000	0.74040100
C	-2.55254300	2.99423200	0.73999300
C	-3.37112600	4.05964000	0.42063000
H	-3.06899100	5.05971300	0.69942700
C	-4.59056600	3.88226300	-0.25355400
H	-5.19562600	4.74961300	-0.47872400
C	-5.03881000	2.63238400	-0.63210800
H	5.97969000	2.49847200	-1.14749200
H	1.61566500	3.12778700	1.26360000
H	-1.61553300	3.12795200	1.26300100
H	-5.97985900	2.49834200	-1.14747700
C	0.00007000	0.84950500	-1.02655000
F	0.00009500	2.17918100	-1.10040100
F	-1.06826900	0.40368800	-1.68656600
F	1.06848000	0.40367000	-1.68644100

Truncated cation of 4a (chloroform)

E = -2000.175769

H = -1999.781507

G = -1999.868875

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C	0.55629400	3.18057300	0.00000000
C	0.63046900	1.09925600	1.19019100
C	0.63046900	1.09925600	-1.19019100
C	0.57191800	2.48425800	-1.19589300
C	0.57191800	2.48425800	1.19589300
H	0.53556300	3.00364500	-2.14489300
H	0.53556300	3.00364500	2.14489300
C	-0.45705900	-0.03322800	3.10896200
N	-0.09169100	-0.54222700	4.27866000
C	-0.45705900	-0.03322800	-3.10896200
N	-0.09169100	-0.54222700	-4.27866000
I	-2.36528000	0.07952600	2.36796500
I	-2.36528000	0.07952600	-2.36796500
C	-0.92784800	-1.16102600	5.30176600
H	-0.60216800	-2.19022000	5.44025600
H	-1.96670300	-1.14317000	4.98897300
H	-0.81201100	-0.60280700	6.22862900
C	-0.92784800	-1.16102600	-5.30176600
H	-0.60216800	-2.19022000	-5.44025600
H	-0.81201100	-0.60280700	-6.22862900
H	-1.96670300	-1.14317000	-4.98897300
H	0.51554800	4.26115900	0.00000000
C	1.74092300	0.24385400	3.26496700
C	1.28490900	-0.38794400	4.41519200

C	1.74092300	0.24385400	-3.26496700
C	1.28490900	-0.38794400	-4.41519200
N	0.62124100	0.44197500	2.46173700
N	0.62124100	0.44197500	-2.46173700
C	2.14680000	-0.74973300	5.44345500
C	3.48015000	-0.44506800	5.25388400
H	4.19390000	-0.70516200	6.02374200
C	3.93835900	0.19118100	4.08770800
H	4.99407200	0.40532800	3.98870600
C	3.08068100	0.54734700	3.06542300
C	3.08068100	0.54734700	-3.06542300
C	3.93835900	0.19118100	-4.08770800
H	4.99407200	0.40532800	-3.98870600
C	3.48015000	-0.44506800	-5.25388400
H	4.19390000	-0.70516200	-6.02374200
C	2.14680000	-0.74973300	-5.44345500
H	1.79133600	-1.24582000	6.33639300
H	3.42749600	1.03573700	2.16483700
H	3.42749600	1.03573700	-2.16483700
H	1.79133600	-1.24582000	-6.33639300
C	0.78026900	-1.14630800	0.00000000
F	1.42159800	-1.61823100	1.06741600
F	1.42159800	-1.61823100	-1.06741600
F	-0.44432400	-1.68667500	0.00000000

5. References

[1] F. Heinen, E. Engelage, A. Dreger, R. Weiss, S. M. Huber, *Angew. Chem. Int. Ed.* **2018,** *14*, 3830–3833; *Angew. Chem.* **2018,** *14*, 3892–3896;

[2] J.-P. Gliese, S. H. Jungbauer, S. M. Huber, *Chem. Commun.* **2017,** *88*, 12052–12055.

[3] S. H. Jungbauer, S. M. Huber, *J. Am. Chem. Soc.* **2015,** *37*, 12110–12120.

[4] P. Wipf, Y. Aoyama, T. E. Benedum, *Org. Lett.* **2004,** *20*, 3593–3595.

[5] M. P. Muñoz, M. Méndez, C. Nevado, D. J. Cárdenas, A. M. Echavarren,

Synthesis **2003,** *18*, 2898–2902.

[6] P. Wonner, L. Vogel, M. Düser, L. Gomes, F. Kniep, B. Mallick, D. B. Werz,

S. M. Huber, *Angew. Chem. Int. Ed.* **2017,** *39*, 12009–12012;

Angew. Chem. **2017,** *39*, 12172–12176

[7] F. Inagaki, C. Matsumoto, Y. Okada, N. Maruyama, C. Mukai,

Angew. Chem. Int. Ed. **2015,** *3*, 818–822; *Angew. Chem.* **2015,** *3*, 832–836.

[8] S. G. Weber, D. Zahner, F. Rominger, B. F. Straub,

Chem. Commun. **2012,** *92*, 11325–11327.

[9] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

[10] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008,** *1-3*, 215–241.

[11] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005,** *18*, 3297–3305.

[12] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010,** *15*, 154104.

[13] E. Engelage, N. Schulz, F. Heinen, S. M. Huber, D. G. Truhlar, C. J. Cramer, *Chem. Eur. J.* **2018,** *60,* 15983–15987.