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Chemie

Supporting Information

Spectroscopic and Computational Evidence of Intramolecular $Au^{I}\cdots H^{+}-N$ Hydrogen Bonding

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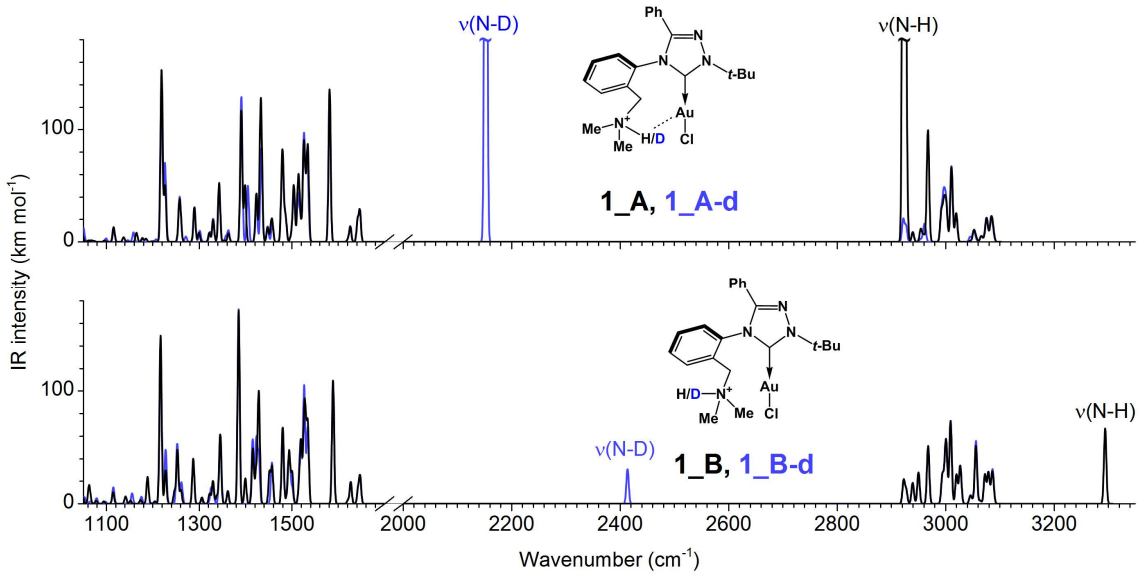


Figure S1. Harmonic vibrational spectra of **1_A** and **1_B** calculated at the B3LYP-D3/6-31G*/Au:def-2SVP level of theory (see Methods). The frequencies below and above 2000 cm^{-1} were scaled by factors of 0.99 and 0.955, respectively.

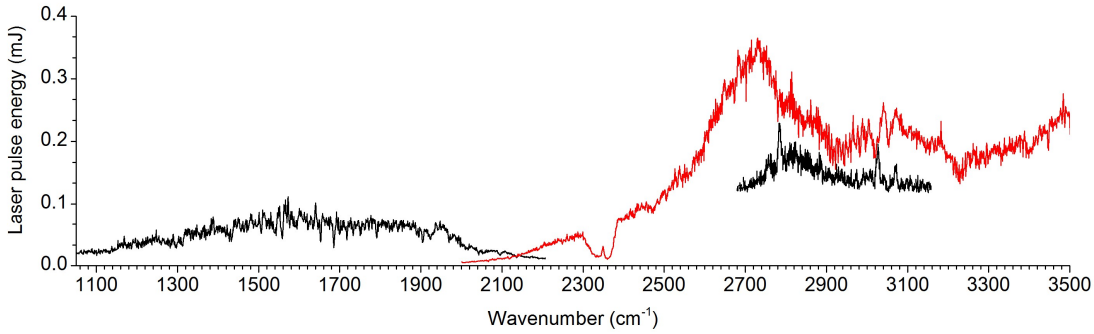


Figure S2. Power output of the IR laser system acquired behind the exit window of the ISORI instrument when acquiring the spectra of 1/1-D. Only a fraction of the laser power was recorded due to electrode geometry, to beam divergence and to absorption by the exit window (5 mm CaF_2). The right trace (ca 3000 cm^{-1}) was clipped because the minimum threshold of the power meter was set to 0.12 mJ. Therefore, we also show a typical energy profile recorded previously (red trace, not to scale).

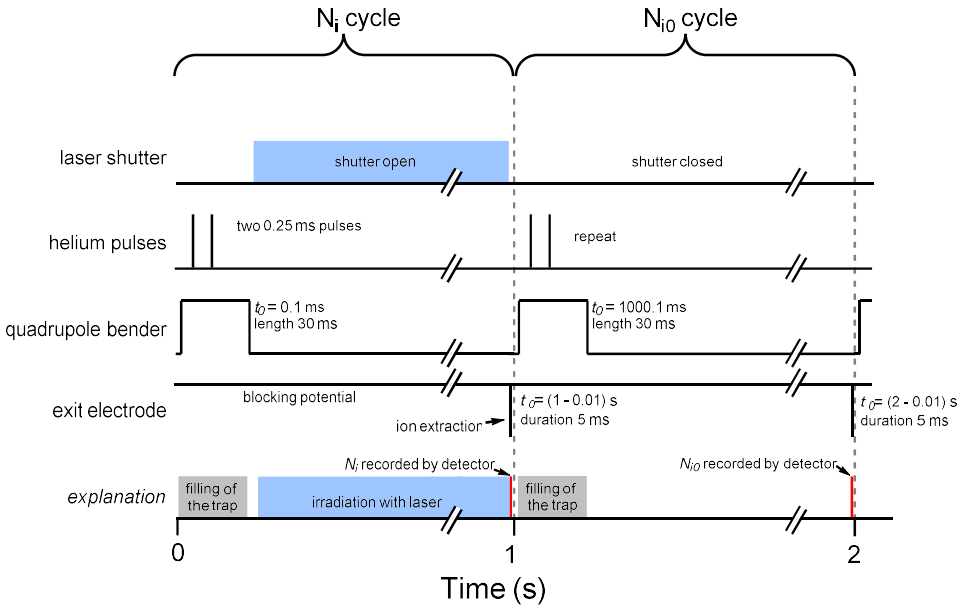


Figure S3. Timing sequence for the acquisition of IRPD and visPD spectra using the ISORI instrument

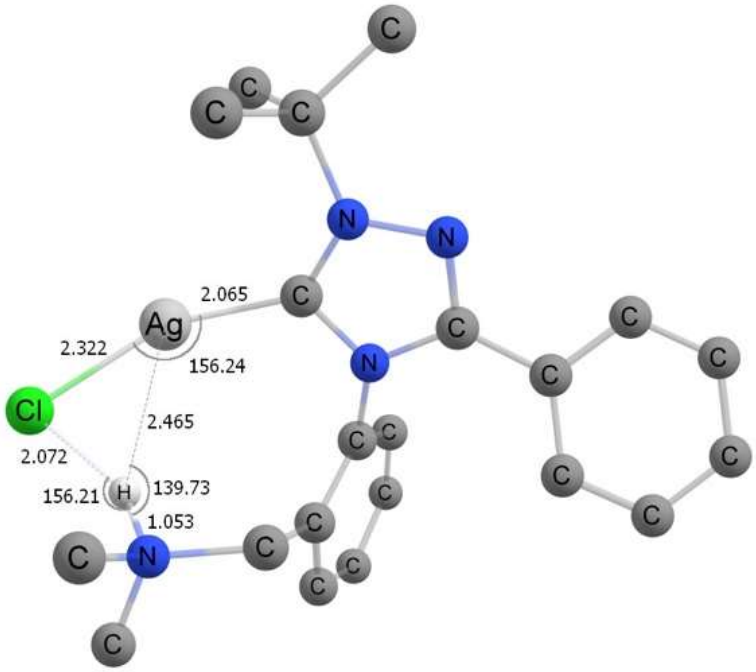
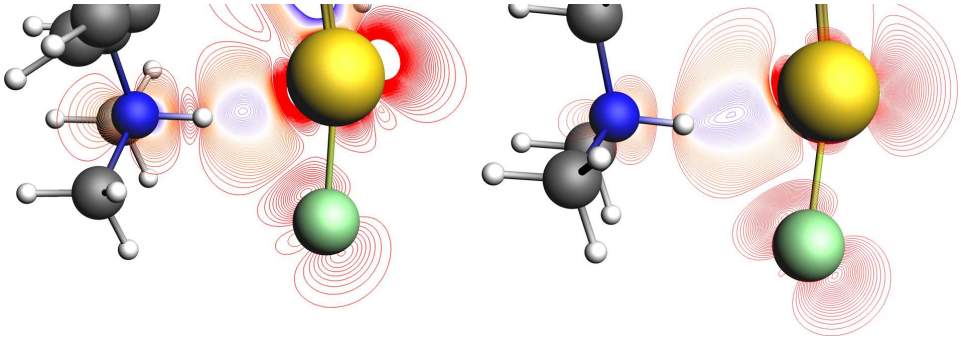


Figure S4. Silver analogue of system S1 calculated at PBE0-D3/def2-TZVPP level.



1_A **2**

Figure S5: Differential ETS–NOCV electron densities of Au···H^+–N interaction channels in **1_A** and **2.** The blue/red color indicates increased/decreased electron density between corresponding atoms

Table S1. Selected structural parameters of **1_A** calculated at different computational levels

System 1								
Level	Basis set	M–H	N–H	M–N	M–H–N	C–M–Cl	H–Cl	Cl-H-N
SCS-MP2	def2-TZVPP	2.137	1.041	3.134	160	170	2.483	142
PBE0-D3	def2-TZVPP	2.165	1.045	3.163	159	169	2.494	142
B3LYP	def2-SVP	2.142	1.045	3.163	165	168	2.636	136
B3LYP	6-31G*/ Au:def-2SVP	2.168	1.045	3.189	165	169	2.636	137
PBE0-D3	6-31G*/ Au:def2SVP	2.158	1.046	3.172	163	169	2.572	139
PBE0-D3	def2-TZVPP PCM	2.281	1.037	3.295	166	179	3.624	135
PBE0	def2-TZVPP	2.225	1.044	3.204	155	169	2.446	146

Table S2. Energy differences between geometry optimized **1_A** and **1_B** (Figure 1 in main text) at selected computational levels. All values are expressed as kcal/mol

level	E(**1_A**) – E(**1_B**)
HF/def2-TZVPP	-9.4
SCS–MP2/def2-TZVPP	–11.7
PBE0–D3/def2-TZVPP	–11.0
PBE0-D3/def2-TZVPP(PCM)	-4.2

Table S3. Summary of the distances and QTAIM parameters at bond critical points (if found) of selected atoms pairs in **1_A** and **1_B.** Geometries at PBE0/def2-TZVPP level. All QTAIM parameters are calculated at the ZORA PBE0/TZP level

1_A

A···B	$r_{A\cdots B}$	ϱ	Laplacian	DI
Au···H(N)	2.17	0.033	0.076	0.13
Au···H(tBu)	2.71/2.85	0.013/0.010	0.039/0.031	0.06/0.05
Cl···H(N)	2.5	No LCP	No LCP	0.04

1_B

A···B	$r_{A\cdots B}$	ϱ	Laplacian	
Au...H(CH_2)	2.54	0.019	0.051	0.08
Au···H(t-Bu)	2.66/2.78	0.014/0.012	0.043/0.035	0.06/0.05
Cl···H(MeN)	2.45/2.99	0.016/0.006	0.050/0.019	0.08

Coordinates of the calculated systems, all at PBE0-D3/def2-TZVPP level.

System 1_A

```
54
AuC21N4H27Cl
C       -0.027430000      0.964709000     -0.190745000
N        1.047751000      0.124128000     -0.152117000
C        2.171208000      0.872660000      0.145937000
N        1.821926000      2.114629000      0.308725000
N        0.490073000      2.156236000      0.095489000
C        3.547532000      0.398255000      0.251577000
C        4.572690000      1.284312000     -0.083262000
C        5.894155000      0.890627000      0.026607000
C        6.206879000     -0.386287000      0.472277000
C        5.191916000     -1.268256000      0.813514000
C        3.867062000     -0.881306000      0.704401000
C        1.049490000     -1.236127000     -0.595737000
C        1.633149000     -1.484450000     -1.828259000
C        1.765969000     -2.780701000     -2.293548000
C        1.334632000     -3.837780000     -1.508662000
C        0.748362000     -3.585370000     -0.280426000
C        0.566529000     -2.286828000      0.192816000
Au      -1.900195000      0.341226000     -0.431593000
Cl      -3.938771000     -0.663872000     -0.398732000
C       -0.242571000      3.453218000      0.229221000
C        0.774976000      4.566961000      0.419092000
C       -0.072802000     -2.074987000      1.532985000
N       -1.576076000     -2.129761000      1.517031000
C       -2.151515000     -3.431066000      1.113095000
C       -1.153109000      3.360429000      1.448285000
C       -1.041495000      3.696438000     -1.045157000
C       -2.138078000     -1.670413000      2.806983000
H        1.997474000     -0.648866000     -2.412216000
H        7.241995000     -0.693288000      0.555689000
H        0.254613000     -2.835098000      2.244151000
H        0.183183000     -1.095744000      1.935853000
H        1.460454000     -4.858217000     -1.847021000
H       -3.221073000     -1.630419000      2.712969000
H       -1.757941000     -0.673891000      3.022714000
H       -1.847420000     -2.364670000      3.593878000
H        3.087833000     -1.577709000      0.983943000
H        4.321422000      2.278296000     -0.430170000
H        0.437647000     -4.419843000      0.337415000
H        5.432776000     -2.261517000      1.171047000
H        6.683565000      1.582214000     -0.239416000
H        2.222346000     -2.962638000     -3.257938000
H        1.363932000      4.429944000      1.324299000
H        0.229600000      5.507398000      0.498030000
H        1.458095000      4.635311000     -0.427022000
H       -1.803268000     -3.683973000      0.116182000
H       -3.233310000     -3.322674000      1.090404000
H       -1.854797000     -4.193911000      1.831953000
H       -1.902403000      2.576298000      1.328224000
H       -1.676178000      4.307774000      1.580379000
H       -0.572033000      3.163696000      2.351042000
H       -0.387789000      3.712244000     -1.918277000
H       -1.538352000      4.663962000     -0.971842000
H       -1.811510000      2.939149000     -1.198465000
```

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H       -1.895313000     -1.437127000      0.803309000
```

System 1_B

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AuC21N4H27Cl
C       -0.263911000     -2.121630000     -0.085034000
C        0.287790000     -1.105600000     -0.870904000
C        0.993777000     -1.416106000     -2.025306000
C        1.197904000     -2.731748000     -2.397500000
C        0.715090000     -3.751573000     -1.593361000
C       -0.005931000     -3.439857000     -0.453972000
N        0.285428000      0.270804000     -0.481327000
C       -0.769175000      1.142377000     -0.514777000
N       -0.199463000      2.329712000     -0.307940000
N        1.136700000      2.254760000     -0.134945000
C        1.439857000      0.998213000     -0.245502000
Au      -2.699458000      0.667573000     -0.579558000
Cl      -4.878974000      0.052269000     -0.405424000
C        2.802211000      0.483413000     -0.134820000
C        3.848076000      1.285271000     -0.592141000
C        5.157203000      0.852319000     -0.475189000
C        5.435556000     -0.379583000      0.100261000
C        4.399284000     -1.176768000      0.565132000
C        3.087536000     -0.750161000      0.449058000
C       -0.874038000      3.663207000     -0.212160000
C       -1.726013000      3.874283000     -1.457526000
C       -1.086899000     -1.816505000      1.129427000
N       -2.299478000     -2.701466000      1.297255000
C       -3.172008000     -2.142962000      2.369485000
C        0.196924000      4.740916000     -0.138783000
C       -1.720124000      3.681919000      1.055533000
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H        0.894071000     -4.787050000     -1.852761000
H       -3.954584000     -2.863618000      2.596341000
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H       -3.579692000     -2.013548000     -0.237189000
H       -3.879614000     -3.675024000      0.325382000
H       -2.475063000     -3.337225000     -0.720606000
H       -2.510030000      2.930128000      1.021620000
H       -2.190761000      4.659978000      1.158318000
H       -1.100387000      3.507287000      1.936737000
H       -1.116746000      3.815607000     -2.360606000
H       -2.176033000      4.866169000     -1.411983000
H       -2.533883000      3.145707000     -1.532603000
H       -1.961681000     -3.607047000      1.617585000
```

Ag analogue of 1_A

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54
AgC21N4H27Cl
C       -0.012781000      1.029432000     -0.286779000
N        1.047281000      0.175014000     -0.228338000
C        2.173623000      0.892430000      0.132061000
N        1.837974000      2.136119000      0.316026000
N        0.515176000      2.199528000      0.051466000
C        3.538278000      0.393260000      0.273614000
C        4.587877000      1.278368000      0.021103000
C        5.898737000      0.861747000      0.166505000
C        6.177549000     -0.438135000      0.566039000
C        5.138554000     -1.319875000      0.824944000
C        3.823971000     -0.909729000      0.680011000
C        1.023685000     -1.181237000     -0.682525000
C        1.619958000     -1.435601000     -1.908062000
C        1.726464000     -2.731086000     -2.380975000
C        1.262357000     -3.781153000     -1.605511000
C        0.667549000     -3.523163000     -0.382602000
C        0.499694000     -2.223244000      0.093147000
Ag      -1.934498000      0.345439000     -0.605609000
Cl      -3.754566000     -1.073921000     -0.352054000
C       -0.214133000      3.492380000      0.206940000
C        0.800818000      4.606090000      0.409685000
C       -0.125163000     -1.984271000      1.437693000
N       -1.610608000     -2.207338000      1.522112000
C       -2.032741000     -3.620099000      1.393874000
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C       -1.021785000      3.752781000     -1.058113000
C       -2.144197000     -1.611449000      2.768778000
H        2.015015000     -0.604916000     -2.478963000
H        7.204524000     -0.763156000      0.677248000
H        0.317998000     -2.640000000      2.190476000
H        0.039303000     -0.955151000      1.751279000
H        1.373014000     -4.802929000     -1.945212000
H       -3.226125000     -1.720965000      2.765469000
H       -1.892315000     -0.552993000      2.789002000
H       -1.710020000     -2.120235000      3.628292000
H        3.026283000     -1.607925000      0.894922000
H        4.363434000      2.290271000     -0.290477000
H        0.350982000     -4.358071000      0.229721000
H        5.352080000     -2.331843000      1.145562000
H        6.706701000      1.553523000     -0.035757000
H        2.191165000     -2.919039000     -3.340209000
H        1.390332000      4.458294000      1.312690000
H        0.256557000      5.546266000      0.499119000
H        1.483933000      4.682831000     -0.435954000
H       -1.769232000     -3.984953000      0.406116000
H       -3.114523000     -3.655626000      1.499276000
H       -1.554265000     -4.215577000      2.170536000
H       -1.864429000      2.586062000      1.292955000
H       -1.652517000      4.314871000      1.578245000
H       -0.537792000      3.164344000      2.324373000
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H       -1.790147000      2.994918000     -1.217694000
H       -2.114867000     -1.710951000      0.741912000
```

Model 2

```
19
AuC4NH12Cl
C       -0.027430000      0.964709000     -0.190745000
H        0.828041000      0.549462000     -0.728343000
H        0.272697000      1.703397000      0.556204000
H        0.321810000     -2.251182000      0.536722000
Au      -1.900195000      0.341226000     -0.431593000
Cl      -3.938771000     -0.663872000     -0.398732000
C       -0.072778000     -2.074997000      1.532938000
N       -1.576076000     -2.129765000      1.517040000
C       -2.151515000     -3.431065000      1.113092000
C       -2.138078000     -1.670420000      2.806986000
H        0.254593000     -2.835083000      2.244176000
H        0.183179000     -1.095746000      1.935859000
H       -3.221073000     -1.630419000      2.712969000
H       -1.757941000     -0.673891000      3.022714000
H       -1.847420000     -2.364670000      3.593878000
H       -1.803268000     -3.683973000      0.116182000
H       -3.233310000     -3.322674000      1.090404000
H       -1.854797000     -4.193911000      1.831953000
H       -1.895313000     -1.437120000      0.803316000
```

CN2 analogue of Model2

```
 19


 C    -0.027430     0.964709    -0.190745
 N     1.181378     0.895002     0.417540
 N     1.017608     1.777616    -0.495117
 Au   -1.900195     0.341226    -0.431593
 Cl   -3.938771    -0.663872    -0.398732
 H     0.322460    -2.250674     0.536954
 C    -0.072802    -2.074987     1.532985
 N    -1.576076    -2.129761     1.517031
 C    -2.151515    -3.431066     1.113095
 C    -2.138078    -1.670413     2.806983
 H     0.254613    -2.835098     2.244151
 H     0.183183    -1.095744     1.935853
 H    -3.221073    -1.630419     2.712969
 H    -1.757941    -0.673891     3.022714
 H    -1.847420    -2.364670     3.593878
 H    -1.803268    -3.683973     0.116182
 H    -3.233310    -3.322674     1.090404
 H    -1.854797    -4.193911     1.831953
 H    -1.895313    -1.437127     0.803309
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Model 3

```
46
AuC15N4H25Cl
H       -3.221073000     -1.630419000      2.712969000
H       -1.757941000     -0.673891000      3.022714000
H       -1.847420000     -2.364670000      3.593878000
C       -2.138077000     -1.670437000      2.806992000
```

N	-1.576076000	-2.129771000	1.517043000
H	-1.895314000	-1.437111000	0.803325000
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H	-3.233310000	-3.322674000	1.090404000
H	-1.854797000	-4.193911000	1.831953000
H	-1.803268000	-3.683973000	0.116182000
C	-0.072804000	-2.074873000	1.532909000
H	0.183208000	-1.095744000	1.935838000
H	0.307701000	-2.286227000	0.542051000
H	0.254594000	-2.835117000	2.244140000
N	1.047785000	0.124003000	-0.152000000
C	-0.027445000	0.964692000	-0.190718000
N	0.490072000	2.156235000	0.095493000
N	1.821934000	2.114638000	0.308674000
C	2.171179000	0.872716000	0.145903000
Au	-1.900194000	0.341227000	-0.431599000
Cl	-3.938771000	-0.663872000	-0.398733000
C	3.547529000	0.398251000	0.251598000
C	4.572690000	1.284312000	-0.083261000
C	5.894155000	0.890627000	0.026608000
C	6.206879000	-0.386287000	0.472278000
C	5.191916000	-1.268256000	0.813514000
C	3.867062000	-0.881306000	0.704401000
C	-0.242571000	3.453218000	0.229222000
C	-1.041495000	3.696438000	-1.045156000
C	0.774976000	4.566961000	0.419093000
C	-1.153109000	3.360429000	1.448286000
H	7.241995000	-0.693288000	0.555690000
H	3.087833000	-1.577709000	0.983943000
H	4.321422000	2.278296000	-0.430169000
H	5.432776000	-2.261517000	1.171047000
H	6.683565000	1.582214000	-0.239415000
H	1.363932000	4.429944000	1.324300000
H	0.229600000	5.507398000	0.498031000
H	1.458095000	4.635311000	-0.427021000
H	-1.902403000	2.576298000	1.328224000
H	-1.676178000	4.307774000	1.580380000
H	-0.572033000	3.163696000	2.351043000
H	-0.387789000	3.712244000	-1.918276000
H	-1.538352000	4.663962000	-0.971841000
H	-1.811510000	2.939149000	-1.198464000
H	1.053572000	-0.805625000	-0.526180000